Evidence for magmatic vapor deposition of anhydrite prior to the 1991 climactic eruption of Mount Pinatubo, Philippines

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ABSTRACT

Anhydrite (CaSO4) phenocrysts from Mount Pinatubo pumices show evidence of having responded dynamically to changing conditions prior to the June 15, 1991 climactic eruption. Micrometer-sized and smaller pyramidal surface growth features and lesser numbers of etch pits on anhydrite surfaces are documented by scanning electron microscopy. Chemical analyses indicate that the pyramids are a CaSO4 polymorph and electron backscatter diffraction patterns show conclusively that the pyramids are indeed orthorhombic anhydrite and not another Ca-sulfate phase. Unit-cell measurements of volcanic anhydrite are identical with evaporitic anhydrite, as determined from single-crystal X-ray diffraction patterns.

The computer program SOLVGAS was used to identify conditions under which the pyramids may have precipitated. Thermodynamic modeling of a cooling magmatic gas (H2O-CO2-SO2) at 500 bars (maximum model pressure) and NNO +1.7 was performed. Assuming that the gas contained >10^-9 mol% Ca and 4 mol% SO2, the program indicates that anhydrite will precipitate homogeneously at approximately 780 °C, whereas an isothermal drop in pressure would likely lead to dissolution. Pyramids located between a phenocryst and adjacent glass provide physical evidence that at least a portion of the pyramids nucleated and grew before the melt quenched.

We propose a mechanism to account for these previously unrecognized surface growths, which is that the anhydrite pyramids precipitated from a fluid or vapor phase that had separated from the magma at depth. At least a portion of the Pinatubo anhydrite phenocrysts provided substrates for nucleation and epitaxial growth of anhydrite. Because the anhydrite pyramids resemble products of chemical vapor deposition of metals and ceramics, we propose that this previously unrecognized process be termed magmatic vapor deposition. Evidence of high-temperature, magmatic vapor deposition of anhydrite could be used as an indicator that a pre-eruptive gas phase was accumulating or stored at depth, especially at arc volcanoes where excess amounts of sulfur are vented into the atmosphere.

INTRODUCTION

Background

In 1982, El Chichon volcano in Mexico erupted, releasing a massive SO2-rich plume, raising consciousness of the potential impact of S-rich volcanic eruptions upon climate (Sigurdsson 1990). Anhydrite (CaSO4) was found in the pumices, alerting scientists to the fact that anhydrite can be a magmatic phase (Luhr et al. 1984). Petrologists have since studied anhydrite-melt phase equilibria (Carroll and Rutherford 1987; Luhr 1990; Evans and Scaillet 1997; Scaillet et al. 1998; Scaillet and Evans 1999) and also found magmatic anhydrite at other volcanoes where sulfate-rich plumes are present such as Nevado del Ruiz (Fournelle 1990) and Mount Pinatubo. It has been predicted experimentally that anhydrite may exist in plutonic rocks (Baker and Rutherford 1996). This hypothesis was recently confirmed after anhydrite was found in granitic rocks at Cajon Pass, California (Barth and Dorais 2000).

Phenocrystic anhydrite in andesite or dacite pumices is rarely observed owing to rapid sub-aerial weathering (Arculus et al. 1983). One year after the El Chichon eruption, whole-rock sulfur values had decreased by 80%, due to dissolution of anhydrite by meteoric water (Luhr et al. 1984).

Mount Pinatubo pumice: chemistry and mineralogy

Beginning in mid-March 1991, Mt. Pinatubo, a composite volcano within the Luzon volcanic arc in the Philippines, underwent a period of shallow volcano-tectonic earthquakes, phreatic explosions, buildup of a lava dome, and explosive eruptions producing pyroclastic flows and surges (Wolfe and Hoblitt 1996). These events culminated with a nine-hour eruption on June 15, 1991, the 20th century’s second most volumetric volcanic eruption, which released the largest observed SO2 cloud into the stratosphere, approximately 20 megatons (Bluth et al. 1992). Various hypotheses were presented to account for the excess S vented and are reviewed in the discussion section.

Anhydrite phenocrysts were soon discovered in Mt. Pinatubo...
pumice (Bernard et al. 1991; Fournelle 1991) and at least 12 papers in the Mt. Pinatubo Fire and Mud monograph (Newhall and Punongbayan 1996) discussed this anhydrite.

To date, no one has examined the crystal chemistry of the Pinatubo (or other volcanic) anhydrite. Virtually all the sulfur in the pumice is in the anhydrite, and some investigations have suggested that anhydrite breakdown is significant in the production of the erupted SO$_2$. Additionally, gas modeling has assumed that the anhydrite in the pumice is orthorhombic β-CaSO$_4$. This study focuses on a detailed examination of the Pinatubo anhydrite and the surface features discovered in the course of our research.

Pallister et al. (1996, p. 726) summarized some important features of the Pinatubo anhydrite:

“...anhydrite occurs primarily as subhedral to euhedral crystals in the June 12 scoria and June 15 pumice. It typically includes apatite microcryst and, as at El Chichon (Luh et al. 1984), it is found in growth contact with apatite phenocrysts. Anhydrite is only rarely found in growth contact with silicate phenocrysts.” They suggested that “these relations are consistent with [anhydrite] growth mainly from a separate fluid phase in the magma.”

Pasteris et al. (1996) evaluated inclusions in the Pinatubo dacite phenocrysts, paying particular attention to the liquid and vapor phases. They suggested that the magma may have reached saturation with an H$_2$O-CO$_2$-SO$_2$ supercritical fluid before the melt reached anhydrite saturation, stripping the melt of much of its sulfur, and that in most regions of the magma “anhydrite reached saturation only after quartz phenocrysts had begun to precipitate, meaning that anhydrite was a late phenocryst phase,” p. 885.

Pumices from the dacitic pyroclastic-flow and -fall deposits from the June 15, 1991, Mt. Pinatubo eruption were classified by phenocryst abundance into two groups (Imai et al. 1996). Type 1 is white in color and phenocryst-rich (≥20%): whereas type 2 is yellowish in color and phenocryst-poor (≤20%). Even though the type 2 pumices are phenocryst-poor samples, they contain abundant microscopic crystal fragments (J. Pallister, personal communication 2001). The pumices sampled in this study, labeled P4 and P2, are type 1 (Fournelle et al. 1996).

Phenocrysts are principally plagioclase and hornblende, with lesser amounts of cummingtonite, biotite, quartz, ilmenite, magnetite, apatite, anhydrite, and zircon. Overall, the bulk-chemical composition and Fe-Ti oxide temperatures of the two pumice types are similar (Pallister et al. 1996). The S contents of the pumices are variable. Fournelle et al. (1996) attributed this to the variable distribution of anhydrite phenocrysts within the magma. The whole-rock S content of sample P4 is 900 ppm, lower than the 1200 ppm in pumice P2. Chris Newhall (personal communication 1991) collected sample P2 from an upper layer of a pyroclastic-flow deposit one month after the eruption. It was thus exposed to a month of rainfall, and may have originally had more S (Fournelle et al. 1996). Whole-rock S values for both samples are lower than similar samples reported by Bernard et al. (1991) and Pallister et al. (1996), i.e., 1500–2400 ppm.

Anhydrite phenocrysts are sparse in the June 15 Mt. Pinatubo pumice, ~0.1 vol% according to Bernard et al. (1996). Over 97 wt% of the S in the pumice is in the form of sulfate (Fournelle et al. 1996). Euhedral anhydrite phenocrysts are parallelepiped (450 × 550 × 200 to 250 × 250 × 100 μm) or rectangular in section (100 × 600 × 50 to 100 × 300 × 50 μm).

Subhedral to euhedral anhydrite crystals are surrounded by sharp contacts with vesicular matrix glass (Figs. 1a and 1b) (Bernard et al. 1991; Pallister et al. 1996; Fournelle et al. 1996). Several examples of anhydrite trapped within silicate minerals, specifically hornblende and plagioclase phenocrysts, were found (Figs. 1a, 1c, and 1d) and cited by Fournelle et al. (1996) as evidence that anhydrite was a primary magmatic phase at depth.

Identical $^{87}$Sr/$^{86}$Sr ratios (~0.7042) of anhydrite and bulk-rock confirm that the anhydrite was not sedimentary (Hattori 1996). The ion microprobe study of McKibben et al. (1996) found a unimodal frequency of δS values averaging near +7 per mil in the June 15 eruption anhydrite, indicating that the (SO$_4$)$_2$ component in the melt was isotopically uniform and well mixed. On the other hand, anhydrite phenocrysts from the June 12, 1991 Plinian eruption have a bimodal distribution in δS values (+6.5 and +10.5 per mil). The Sr and S isotope data suggest that most of the anhydrite in the June 15 pumices was not derived from hydrothermal or evaporitic anhydrite deposits in the crust below the volcano.

In their evaluation of the remotely sensed SO$_2$ emitted by Mt. Pinatubo, as well as melt inclusion data and other constraints, Westrich and Gerlach (1992), Wallace and Gerlach (1994) and Gerlach et al. (1996) suggested that most magmatic S had partitioned into a water-rich vapor phase at depth some time prior to the climactic eruption. A similar conclusion was reached by Pasteris et al. (1996). Gerlach et al. (1996) estimated that S preferentially partitioned into the vapor compared to the melt by a factor of ~720, and Wallace (2000) calculated ~950.

Apatite within and adjacent to anhydrite has been observed in thin section, and in microprobe and SEM images [Figs. 1a–1d; Fournelle et al. (1996)]. Most apatite inclusions occur as well-developed hexagonal pinacoids and hexagonal prisms.

Objective of this study

A previous scanning electron microscope (SEM) examination of Pinatubo clasts indicated small hexagonal crystals on the surface of plagioclase in a pumice vesicle (Fournelle et al. 1996; their Fig. 9). Energy-dispersive spectrometry (EDS) Kα peaks of Ca and S suggested that the surface features were a Ca-sulfate phase. The hexagonal shape seemed to conflict with the orthorhombic symmetry of anhydrite. T. Gerlach (personal communication 1992) suggested that X-ray diffraction analysis of Mt. Pinatubo volcanic anhydrite was needed to verify that the appropriate thermodynamic properties were being used in gas modeling. An early observation in our current study was the unexpected existence of micrometer-scale pyramids upon the anhydrite phenocrysts.

The goal here is to describe and identify these surface features on the crystal faces of anhydrite phenocrysts from two June 15, 1991, Mt. Pinatubo pumice samples. We consider whether the pyramids are orthorhombic (β) anhydrite, and not another Ca-sulfate phase such as α-CaSO$_4$, γ-CaSO$_4$, CaSO$_4$,
0.5H₂O (hemihydrate or bassanite), or CaSO₄·2H₂O (gypsum) (Table 1). This is the first SEM study to examine anhydrite phenocryst surfaces.

The computer program SOLVGAS is used here to model possible magmatic conditions for homogeneous anhydrite precipitation or resorption involving vapor. This has important implications for the question of whether or not the Pinatubo system contained a pre-eruptive gas phase prior to the climactic eruption. Overall, this study addresses the Pinatubo budget, taking into account the observed Ca-S surface features.

METHODS

Sample collection

At 13:42 (local time) June 15, 1991, an explosion marked the beginning of a nine-hour eruptive event at Mount Pinatubo (Wolfe and Hoblitt 1996). Pumice sample P4 was collected at 19:30 (local time) by a resident from a pumice-fall layer atop a roof in Angeles City, approximately 25 km east of Mount Pinatubo (Rosalinda M. Temprosa, ICLARM, written communication 1991; Fournelle et al. 1996). The eruption coincided with Typhoon Yunya, and thus rain fell on the pumice from the climactic eruption. The prompt collection of sample P4 minimized contact of rainfall with the water-soluble anhydrite. About one month after the June 15 eruption, C. Newhall collected pumice sample P2 from pyroclastic-flow deposits near Clark Air Base (Fournelle et al. 1996).

Sample preparation

Minerals and glass from pumice P4 were separated in September 1991 at the Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland. The pumice was fractured with a hammer and ground by hand with a mortar and pestle. The products were very briefly washed in water to remove fine powder and then dried at low heat on a hot plate.
Minerals were separated from the sieved pumice using heavy liquids and a Franz magnetic separator. Following heavy liquid treatment, the mineral grains were rinsed in acetone, dried, and stored in glass vials at room temperature (air conditioned) in a cardboard box until September 1998 when this project was initiated. Pumice sample P2 was embedded in epoxy prior to thin section preparation in September 1991, where it briefly was in contact with water.

Anhydrite crystals were individually selected from the nonmagnetic 2.90–3.27 g/cm³ split with the aid of a low-power binocular microscope. The split also held muchapatite. Anhydrite crystals were initially distinguished by cleavage, crystal shape, and color. They are mostly white or colorless, and are orthorhombic with three perfect to good cleavages. Euhedral to quasi-square grains were selected. Crystals were in the 200–600 μm length range.

Analytical techniques

Crystals were placed on two-sided adhesive tape atop a microscope slide and carbon coated. A Cameca SX51 electron microprobe at the Department of Geology and Geophysics, University of Wisconsin-Madison, was used initially to distinguish anhydrite from other mounted phases, mainlyapatite, and from glass-covered grains. Crystals were imaged by secondary (SE) and back-scattered electrons (BSE). Energy dispersive spectrometry (EDS) was used for qualitative identification and wavelength dispersive spectrometry (WDS) for quantitative analyses. Electron probe microanalysis (EPMA) conditions were 15 kV accelerating voltage, beam currents ranging from 2–10 nA, and a 5–10 μm spot size.

EPMA of anhydrite requires special attention. Normal analytical conditions of a tightly focused beam, with 10 or 20 nA Faraday cup current, at 15 keV accelerating voltage, and 10 s count periods, resulted in variable X-ray intensity measurements for Ca and S (and O when it was measured). This variability was not seen when acquiring X-ray counts on barite (BaSO₄) and celestine (SrSO₄) standards. This behavior with anhydrite is similar to that observed in silicate glasses, alkali feldspar, and apatite under some conditions. It apparently results from some combination of factors such as buildup of a temperature gradient and/or a space-charge layer (Spray and Rae 1995), and perhaps thermal decomposition such as is observed for calcite (Reed 1996).

To minimize the errors in X-ray intensity measurements of Ca and S on both the standard (UW-Geology collection no. 8912A, evaporitic anhydrite from Bancroft, Ontario, Canada) and the unknowns, we reduced the Faraday cup current to 2 nA and expanded the beam spot size to 10 μm. With these conditions, we achieved reproducible and precise results.

High-resolution LEO scanning electron microscopes (Models 982 and 1530) at the Department of Materials Science and Engineering, University of Wisconsin-Madison, were used for most high-resolution imaging of the anhydrite. Crystals that had been carbon coated were additionally platinum or gold coated, and then examined using 3–10 keV, 100 pA at a working distance of 4–6 mm. A NORAN EDS thin-window detector was used to identify some phases.

Electron backscatter diffraction patterns (EBSD) were acquired with a Hitachi S-3500N SEM at ThermoNORAN, Middleton, Wisconsin. Operating conditions were a low vacuum 10–15 Pa, 20 keV, 0.8 nA Faraday current, and 70° tilt at a working distance of 23 mm. Acquisition time was 60 s. A 512 × 512 16-bit Peltier-cooled CCD camera was used. The thin section had been briefly polished with Buehler Mastermet 2 colloidal (0.02 μm) silica suspension and then coated with a ~20 Å carbon coat. Long exposure X-ray precession photographs of a Mt. Pinatubo anhydrite phenocryst (550 × 200 × 100 μm) were taken at the Department of Earth and Atmospheric Sciences at Purdue University, West Lafayette, Indiana. Unfiltered CuKα radiation (λ = 1.542 Å) was used at 30 keV and 20 mA for exposures ranging from 48 to 96 h. The crystal was mounted on a glass fiber and initially oriented by examining the crystal faces present. Morphologically, anhydrite tends to be elongate parallel to either the a- or c-axes, yielding prismatic crystals. Final alignment was achieved using orientation photos. A layer line screen was used to eliminate unwanted upper level diffraction. The precession camera links the precession of the crystal to that of the film cassette, thereby allowing for an undistorted picture of the reciprocal lattice (e.g., the scattering pattern of the crystal).

The SOLVGAS computer program, which computes multicomponent chemical equilibria in gas-solid-liquid systems, was used to model possible homogeneous reactions (Symonds and Reed 1993). The program calculates the equilibrium distribution of gas, solid, and liquid species in systems of up to forty-two components as a function of temperature and pressure. Strict oxygen mass balance allows calculation of the oxygen fugacity at any pressure and temperature, and saturation indices, log (Q/K), are computed. Lack of data on nonideal behavior of gases at elevated pressures limits its use to a maximum of 500 bars or 50 MPa (M. Reed, personal communication 2000).

Observations

Background

Volcanic anhydrite has typically been observed microscopically via polished thin sections (Fig. 1) (Luhr et al. 1984; Fournelle 1990; Bernard et al. 1991). In 1991, SEM examination of unpolished Mt. Pinatubo pumice showed the existence of a Ca-S phase residing on plagioclase in a vesicle (Fournelle et al. 1996). The hexagonal shape conflicted with the orthorhombic symmetry of anhydrite (Table 1), and raised the possibility of a more-complicated history of Ca sulfates in the Mt. Pinatubo pumice.

In searching for anhydrite phenocrysts for the XRD study,
several types of surface features were found and are described here for the first time. The primary features of interest are small, oriented, micrometer-sized euhedral pyramids.

**Pyramidal surface features**

On 18 of the 19 Mt. Pinatubo anhydrite phenocrysts examined by SEM, pyramids covered an estimated 10–75% of the surface area of each crystal, depending upon which crystal and which face of the crystal was observable. The presence of these features appears to be crystallographically controlled with preference for {010} and {001}, the larger crystal faces. The features appear as small pyramids, averaging 1–2 μm across the base (Fig. 2). Most pyramids appear to be hexagonal, although some appear to be four-sided. Some of the pyramidal faces appear perfectly smooth, whereas others are covered by smaller features. Hexagonal pyramids with bases as small as 150–400 nm—and possibly smaller—appear also present (Figs. 2e and 2f). A few pyramids were as large as 8 μm across.

EDS spectra (10 keV, 60 s counts) were acquired for the anhydrite substrate (Figs. 3a and 3b) and three pyramids (Figs. 3c and 3e). The electron scattering range in anhydrite at 10 keV is ~0.75 μm, calculated using the Monte Carlo simulation of Joy (1995). This distance is less than the size of the pyramids analyzed, constraining the incident electrons and most generated X-rays to the pyramids. Comparing the EDS spectra of the pyramids with those of the anhydrite substrate, 2 of the 3 pyramids have very similar peak intensities for O(Kα), S(Kα), and Ca(Kα). The third pyramid, however, differed somewhat inconsistently: O(Kα) peak intensity was 166% of the anhydrite, whereas the S(Kα) and Ca(Kα) values were close to (94%) the anhydrite values. Calculations of theoretical X-ray intensity (Armstrong 1988) for the Ca-sulfate phase with the highest oxygen content (gypsum, CaSO₄·2H₂O) indicate that O(Kα) should be 136% greater, and Ca(Kα) and S(Kα) should be 76% and 75% lower than anhydrite. The difference of geometry of the electron beam incident to the pyramids vs. the substrate translates into potentially big differences in X-ray absorption path lengths, making comparisons of O(Kα) difficult. Nevertheless, most of the EDS evidence suggests the pyramids are probably anhydrite or another CaSO₄ polymorph.

WDS was also used to compare the oxygen content of a polished (cross-section) pyramid (Fig. 1e) with that of the substrate anhydrite. The count rates were equivalent, at the 99% confidence level, ruling out the possibility that the pyramid was a hydrated Ca-sulfate phase.

Following the discovery of the pyramids on the unpolished anhydrite phenocrysts, we found pyramids in three previously published images of polished Mt. Pinatubo anhydrite crystals: in Fournelle et al. (1996, their Figs. 7B and 7D shown here as Figs. 1c–1e), and in Hattori (1996, her Fig. 2B).

**Other surface features**

Other surface features are also present and only discernible at high magnification (Fig. 4). They are 40–80 nanometer-sized, not pyramidal, and best described as nanocrystalline. They are not glass fragments, although larger glass fragments are present. Agglomerations of these “fuzzy” nanocrystalline masses are locally as large as 500 × 250 nm.

These features were examined by EDS, which showed spectra unlike the anhydrite phenocrystal or the micrometer-sized pyramidal growth features. Some contained only 3 peaks: C, O, and Au (C and Au = coatings); on one feature, Si and S peaks were detected, possibly from adjacent phases, as observed on Figure 4b. We are unsure of the chemical composition of these nanocrystalline features, beyond that they are not CaSO₄ phases, nor precipitates from the heavy liquids (no Br or I peaks by EDS).

**Etch pits**

Some surfaces of the anhydrite phenocrysts from Mt. Pinatubo exhibit roughly equilateral triangular etch pits (Fig. 5). Large etch pits reach one micrometer in size, medium-size pits are between 200–300 nanometers, and small etch pits are approximately 15–45 nanometers. Etch pit depths are difficult to estimate, but are assumed to be similar to their lateral dimensions. Etch pits predominantly occur on the surface of the anhydrite phenocrystals, although small (~nanometer) etch pits also have been observed on two pyramids atop a phenocryst. The apices of many pyramids are cratered, perhaps as a result of dissolution or incomplete growth.

**Relation of pyramids to melt**

Figure 6 shows the relation among pyramids, the anhydrite phenocrystal substrate, and adjacent vesiculated glass—the pyramids sit directly on the surface of the anhydrite phenocryst, under the frozen melt (vesicle wall). The bubble wall appears to conform to the outline of the perimeter of the pyramids.

**Inclusions within an anhydrite phenocryst**

Two inclusions protruding from an anhydrite phenocrystal have been imaged with the SEM and analyzed with EDS. Both have a rounded dumbbell shape. The first inclusion (Figs. 7a and 7b) has two zones: a smooth surface dotted with micrometer-sized vesicles (glass) and a smooth surface with no vesicles (apatite). The transition between the glass and apatite is sharp.

The second inclusion is dumbbell-shaped (Figs. 7c and 7d). The right side is smooth with a few vesicles and is clearly glass. The surface of the left side is rough, has Fe and O(Kα) peaks, and is interpreted as titanomagnetite. As seen in polished thin sections (Fig. 1), apatite and titanomagnetite are common inclusions in the Pinatubo anhydrite.

**Chemistry of Mt. Pinatubo anhydrite**

The anhydrite phenocrysts discussed here have been analyzed by EPMA (Table 2). We have examined anhydrite from samples P4 and P2, both from the June 15 eruption of Mt. Pinatubo. Previously, only two EPMA analyses of volcanic anhydrite have been published: El Chichon and Mt. Pinatubo. Bernard et al. (1996) found that the Mt. Pinatubo anhydrite had roughly half the S as the El Chichon anhydrite (Luhr et al. 1984). Our results are identical to those of Bernard et al. (1996). We also found apparent Sr heterogeneity within a single crystal.

The concentration level of Ba in the previous studies was at the several hundred ppm level. We have examined Ba in Pinatubo anhydrite and find it to be low—below detection limits (DL). We also examined Se contents, which are low but slightly above DL in one specimen.
**Figure 2.** SEM images displaying the pyramidal surface features on two Mt. Pinatubo anhydrite separates. (a) Low magnification showing widely scattered nature of the features on the upper surface. (b) Higher magnification of (a) from a near perpendicular angle showing the hexagonal pyramids. Note the uniform alignment of edges. (c-f) View of a second anhydrite crystal from a more oblique angle. The features possess hexagonal symmetry, and are evenly nucleated surface growths that apparently have coalesced, forming hexagonal-looking patterns. The apices of some appear hollow ("craters"). Note the presence of both 1–3 micrometer-sized and tens of nanometer-sized pyramids in both b and f.
Electron backscatter diffraction patterns

EBSD patterns were acquired from an anhydrite inclusion within plagioclase in a thin section of pumice P2 (Figs. 1c and 1d). Eleven patterns on the ~100 μm anhydrite crystal and six patterns on two pyramids were obtained, with the most distinct patterns shown in Figure 8. Twenty-eight zone axes were found that corresponded to those of orthorhombic β-CaSO₄ (anhydrite). We found that all of the acquired patterns contain a dominant set of lines that the hexagonal and trigonal polymorphs lack: the (020), (040), and (060) planes. This result thereby rules out γ-CaSO₄ and α-CaSO₄ as plausible phases.

The identical EBSD patterns of pyramids and substrate demonstrate that the pyramids have the same crystallographic orientation, supporting an epitaxial relationship between the anhydrite pyramids and substrate.

Single-crystal X-ray diffraction

Anhydrite of magmatic origin has been examined by XRD for the first time. X-ray diffraction analysis, using precession photographs, was performed to determine the structure of the Pinatubo phenocrystic anhydrite. Unit-cell dimensions were determined from the (h00) and (h0l) layer line photos. For comparison, Table 3 shows several anhydrite unit-cell dimensions.
from the literature along with determinations from this study. Although the $a$ and $b$ dimensions of the anhydrite unit cell are almost equal, the structure is not pseudotetragonal, nor is twinning observed.

Exposure times for our precession photos ranged from 48 to 96 h (Fig. 9). All spots on the photographs are consistent with anhydrite, which is supportive evidence of epitaxial surface crystals of anhydrite upon the anhydrite phenocryst substrate.

**EXPERIMENT WITH ANHYDRITE**

A short-duration aqueous experiment at moderately elevated temperature (120 °C) was performed to evaluate possible pyramid or etch pit formation in a cooling pumice lump. Anhydrite (evaporative) crystals of 200–400 µm and 400–600 µm sizes from the UW-Madison Geology Collection (no. 8912A) were placed in three small Teflon containers. Anhydrite from the same collection had been used by Fournelle et al. (1996) for a 2-month duration, aqueous-dissolution experiment at room temperature, which showed etch pit development.

One container held a small plastic cap that was filled with 100 µL of distilled water. The second container had a small plastic cap with 100 µL of 2.2 N sulfuric acid. The third container contained only anhydrite crystals. Each container had two small and one large crystal inside it. Tops were placed on the Teflon containers and loosely closed in order to prevent distilled water inside of the autoclave from condensing and dripping onto the anhydrite grains. Some condensation was observed under the top of the Teflon container after the experimental runs, and was most likely a combination of evaporation and condensation of a portion of the original 100 µL of liquid and water leakage due to a semi-open system interaction.

The containers were placed into an autoclave filled with 1.0 L of distilled water and then set to 120 °C and 2.5 bars pressure. The autoclave took 15 to 20 min to reach the desired temperature and pressure. It remained at that setting for 30 min and then degassed under a slow exhaust setting and cooled for another 15 to 20 min. This process was repeated four times, refilling the caps with 100 µL of liquid after the second and third experimental runs. Some of the liquid must have escaped into the autoclave. Crystals were examined and photographed before and after each run with a microscope at magnifications.

**TABLE 2.** EPMA determined chemical compositions of Pinatubo anhydrite, plus other anhydrite compositions

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<th>Pinatubo P2 inclusion in plagioclase</th>
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<td>0.03</td>
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<td>&lt;DL</td>
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<td>57.77</td>
<td>0.02</td>
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<td>57.22</td>
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<td>99.97</td>
<td>99.06</td>
<td>100.24</td>
<td>100.33</td>
<td>99.90</td>
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</table>

Notes: References: Bernard et al. (1996), Luhr et al. (1982). UW probe standard is evaporitic anhydrite. Detection limit (DL) is at the 99% confidence level and is based upon total number of analyses, assuming a homogeneous specimen. ND = no data, NA = not analyzed, no pyr’s = surface free of pyramids.
from 100 to 2000×. The total time the crystals were exposed was between 240 to 280 min.

Two of these processed crystals were selected for SEM examination: a 400–600 μm crystal from inside the container with sulfuric acid and a 200–400 μm grain from inside the container with distilled water. SEM examination revealed no surface features (pyramids or etch pits) on these anhydrite crystals.

**MODELING OF ANHYDRITE – VAPOR EQUILIBRIUM**

**Intensive and extensive parameters**

The presence of surface features on Pinatubo anhydrite phenocrysts—pyramids and etch pits—suggests that melt or vapor was reacting with the anhydrite under pre-, syn-, and/or post-eruptive conditions. The computer program SOLVGAS (Symonds and Reed 1993) was used to model possible magmatic conditions for homogeneous anhydrite precipitation or resorption involving vapor.

The thermochemical database includes anhydrite and gypsum, but not other phases in the CaSO₄-H₂O system (e.g., α-CaSO₄, γ-CaSO₄, or CaSO₄·0.5H₂O). These phases exist at >1200 °C or <150 °C (Chang et al. 1995; see Table 1).

There are no published data for directly sampled gas of the Mt. Pinatubo eruptions. Gerlach et al. (1996) estimated the approximate composition of the major gas species of the pre-eruptive vapor present in the June 15 climactic eruption of Mount Pinatubo, which we have used. They based SO₂ content

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**TABLE 3. Unit-cell dimensions for sedimentary and volcanic anhydrite**

<table>
<thead>
<tr>
<th>Unit-cell dimensions</th>
<th>References</th>
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</thead>
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<tr>
<td>a (Å)</td>
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</tr>
<tr>
<td>b (Å)</td>
<td>6.991(1)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>6.240(1)</td>
</tr>
<tr>
<td>Volume (Å³)</td>
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</table>

Notes: References: 1 = Morikawa et al. (1975), 2 = Hawthorne and Ferguson (1975), 3 = Kirfel and Will (1980), 4 = Mt. Pinatubo anhydrite, this study.
upon remotely sensed satellite data, and H₂O, CO₂, and Cl contents were derived from a combination of experimental calibrations and melt inclusion data. Gerlach et al. (1996) presented two slightly different Pinatubo pre-eruptive gas compositions, which were calculated at 780 °C and ~2750 bars: (1) for P₅₅ = 110 bars: H₂O = 80.1 mol%, CO₂ = 14.5 mol%, SO₂ = 4.0 mol%, and Cl = 1.4 mol%; (2) for P₅₅ = 20 bars: H₂O = 82.9 mol%, CO₂ = 15.1 mol%, SO₂ = 0.8 mol%, and Cl = 1.2 mol%. The pressure values were originally reported as 11 and 2 MPa, respectively, and are here converted to bars.

Gerlach et al. (1996) favored the first gas composition, but we have evaluated both. Using these gas compositions as those coexisting with magma at pre-eruptive conditions, ~2200 bars (220 MPa) is a major assumption with obvious limitations, including that it is an averaged gas composition—any anhydrite phenocryst in the magma could have been in contact with an aliquot of different gas composition compared with that elsewhere in the system. Given these uncertainties, we estimated how much Ca can be added to the gases before they become saturated with anhydrite, at the maximum pressure permitted by SOLVGAS, 500 bars, and follow up with an extrapolation to 2200 bars.

Two key parameters are temperature and oxygen fugacity, constrained by cummingtonite-dacite equilibria and FeTi-oxide determinations. Rutherford and Devine (1996) found the temperature was 780 °C (±10°) and fₒ₂ was NNO + 3.0. However, Evans and Scaillet (1997) presented convincing evidence that fₒ₂ was NNO + 1.7 (±0.2). We model this later value, but also evaluated the higher fₒ₂.

Calcium is a limiting variable in the model calculations for homogeneous precipitation of anhydrite from the gas and must be present for our hypothesized process to work. Isobaric cooling (1000 to 600 °C) simulations using the 110 bars (4 mol%) SO₂ gas composition of Gerlach et al. were performed at 500 bars for NNO + 1.7 and NNO + 3.0, with Ca ranging from 10⁻⁹ to 10⁻⁷ mol%. We searched iteratively for saturation of anhydrite at a temperature of 775–780 °C.

These simulations show that for a gas with 10⁻⁹ mol% Ca, anhydrite is saturated at ~775 °C and NNO + 1.7 (Fig. 10). Similarly, anhydrite saturates in the same gas at NNO + 3.0 at approximately one log unit lower, 10⁻¹⁰ mol% Ca. If we take the alternative gas calculated by Gerlach et al., with 0.8 mol% SO₂ at NNO + 1.7, the requisite Ca value is higher, ~3 × 10⁻⁹ mol%.

Are these values for Ca contents in the Pinatubo gas reasonable? There is the possibility that the ideal gas behavior of the SOLVGAS model used for low pressure (1–500 bars) equilibria is not appropriate for conditions at ~2000 bars, and thus the predicted Ca content of the gas may be different. We attempted to characterize the sensitivity of the Ca content in the gas (required for anhydrite saturation) in order to determine if the Ca saturation limit varies significantly with respect to pressure. The temperature of anhydrite saturation was fixed at 775–780 °C, while the oxygen fugacity was established at NNO + 1.7 for the 4 mol% SO₂ gas composition. The pressure was modeled in roughly 50 bar increments ranging from 50–500 bars (5–50 MPa). An additional point of 750 bars was evaluated to determine if a significant change in Ca saturation occurred, even though it is outside the pressure limitation of the
**Figure 7.** SEM images of inclusions in anhydrite phenocryst. (a) Low-magnification image of bi-lobate inclusion: apatite (below) and vesiculated glass (above). (b) Higher magnification shows two distinct zones: glass vesicles above and smooth-surfaced apatite below. At the interface (arrow), the top of the apatite, there is a wrinkled skin. The apatite has a rounded morphology. (c) Low-magnification image of another bi-lobate inclusion with vesiculated glass inclusion (right) and Fe-oxide (left). (d) Higher magnification showing rough surface of Fe-oxide. Angular feature is glass shard. At the interface, the glass is constricted in a thin “belt”.

**Figure 8.** EBSD patterns collected from a thin section of Pinatubo pumice P2. (a) Pyramid. (b) Anhydrite substrate. (c) Indexed lines and zone axes superimposed upon pattern (b) for anhydrite, orthorhombic CaSO₄. The (020), (040) and (060) occur only in orthorhombic CaSO₄. (d) BSE image of region where EBSD patterns were collected (larger area in Fig. 1d); 1 = pyramid, 2 = anhydrite substrate. Adjacent apatite (Ap) and plagioclase (Pl) indicated. Due to extreme foreshortening, the 5 µm scale refers to lateral scale only. Pattern collection conditions: 70° tilt, 23 mm working distance, 20 keV, 0.8 nA, 10–15 Pa and 60 s collection time.
Figure 9. Long exposure precession photographs. All spots are consistent with anhydrite; no other phase (extra spots) was detected: (a) (hk0), 96 h (b) (h0l), 48 h (c) (hkk), 72 h.

Figure 10. Results of thermodynamic modeling of homogeneous nucleation of anhydrite using the computer program SOLVGAS, showing the effects of $f_{O_2}$, pressure, and $SO_2$ gas content. (a) The estimated Pinatubo gas was cooled from 1000 to $<700$ °C in 10–25° increments at 500 bars, which is the maximum pressure for the model. The anhydrite saturation surface (log $Q/K = 0$, where $Q =$ calculated speciation, $K =$ equilibrium product/reactant ratios) was determined at a range of gas Ca contents, for three different sets of conditions: (1) at 4.0 mol% $SO_2$ and NNO + 1.7; (2) at 0.8 mol% $SO_2$ and NNO + 1.7; and (3) at 4 mol% $SO_2$ and NNO + 3.0. The line indicates the pre-eruptive temperature of 780 °C. A gas with $\sim 1 \times 10^{-10}$ to $3 \times 10^{-9}$ mol% Ca would have precipitated anhydrite. (b) The calculations above for gas (1) with $1 \times 10^{-8}$ mol% Ca at pressures of 500, 150, 100 and 1 bars. An isothermal drop in pressure would put anhydrite out of equilibrium with the surrounding gas, resulting in dissolution. (c) SOLVGAS modeling from 50 to 500 bars for Ca concentration (mol%) necessary to precipitate anhydrite between 775–780 °C at NNO + 1.7, gas 1. A curve through the modeled data is extrapolated to higher pressure suggesting a limiting calcium value of $1 \times 10^{-9}$ mol%.
model (Fig. 10c).

Extrapolating out to greater pressures suggests that the Ca content may reach a constant value near $1 \times 10^{-8}$ mol%. As the pressure increases, the relative amount of Ca required for vapor saturation of anhydrite decreases. Following this assumption, we postulate that the amount of Ca necessary for anhydrite saturation at 2200 bars, the pre-eruptive pressure, is approximately $1 \times 10^{-8}$ and probably not less than $5 \times 10^{-10}$ mol%. This finding suggests that our inferred 500 bar Pinatubo gas Ca concentration is not unreasonable for the higher pressure.

There are not many volcanic gas analyses that include Ca. In one, Symonds and Reed (1993) restored a published Mt. St. Helens gas analysis (Sept. 1981, 710 °C, 1 bar, $4.9 \times 10^{-7}$ mol% Ca) to 100 bar and 930 °C (for G/R, gas/rock = 0.01) and calculated $1.3 \times 10^{-10}$ mol% Ca. For 1 bar and 710 °C (and G/R = 1000), they calculated $1.1 \times 10^{-12}$ mol% Ca.

Holding all but one variable constant, the sensitivity of that variable upon anhydrite saturation temperature near 780 °C (Fig. 10) can be evaluated: (1) if we decrease Ca content by an order of magnitude, the saturation temperature decreases by ~$50^\circ$; (2) if we increase $f_{O_2}$ by 1.3 log units, the saturation temperature increases by ~$50^\circ$; (3) if we decrease pressure from 500 to 250 bars, the saturation temperature drops by ~$10^\circ$; and (4) if we decrease SO$_2$ from 4.0 to 0.8 mol%, the saturation temperature drops by ~$30^\circ$.

**Mass balance**

It has been shown thermodynamically that anhydrite pyramids could have precipitated homogeneously from a reasonable gas composition at 500 bars (50 MPa) and pre-eruptive temperature and $f_{O_2}$. However, given the low concentration of Ca in the putative vapor, we need to estimate if the observed mass of anhydrite pyramids could be accounted for.

How many grams of Ca would be in the estimated 158 Mt ($6.6 \times 10^{12}$ moles) of vapor calculated by Gerlach et al. (1996)? The estimated $1 \times 10^{-8}$ mol% Ca is equivalent to $2.5 \times 10^3$ grams of Ca, a small amount, especially given the volume of total gas vented to the atmosphere. It is important to note that the 158 Mt of vapor is a minimum because of possible scavenging of SO$_2$ on ash (Gerlach, personal communication 2001), and that the Ca concentration was selected from the extrapolation to the pressure assumed for the gas composition.

Assuming a phenocryst size of $200 \times 200 \times 400$ μm, each has a volume of $1.6 \times 10^7$ μm$^3$, and surface area of $4.0 \times 10^8$ μm$^2$. If pyramids cover 20% of the entire surface area, there would be $2.7 \times 10^7$ μm$^3$ of pyramids 1 μm in height per phenocryst. Each phenocryst would contain $2.4 \times 10^8$ grams of Ca in these surface pyramids. The estimated Ca content of the gas would thus be able to cover $10^{13}$ anhydrite phenocrysts with 20% pyramids. This is a large number of phenocrysts and could account for what we have observed. However, if we estimate the total number of anhydrite phenocrysts in the ~5 km$^2$ dense rock equivalent (Scott et al. 1996) of pumice and ash, assuming a uniform distribution of S at 1200 ppm and that 97 wt% of S is sulfate (Fournelle et al. 1996), in addition to the low level of S in the glass and the typical phenocryst size above, there are a much larger number of phenocrysts, over $1 \times 10^{14}$.

The total number of anhydrite phenocrysts is significantly larger, by seven orders of magnitude, than the number we suggest may contain surface pyramids. This implies that only a very small fraction of anhydrite phenocrysts may have experienced the pyramidal epitaxial growth.

**DISCUSSION**

**Low- or high-temperature features?**

Surface features—pyramids and etch pits—on magmatic anhydrite phenocrysts have not been documented previously. Did they form at high temperature, or are they artifacts of post-eruptive, low temperature processes?

The smaller, fuzzy nanofeatures are likely post-eruptive artifacts, similar to ones observed on microspheres of Hawaiian basaltic glass collected during eruption of vents at Kilauea volcano that had been sitting in a lab for a year. The fuzzy features were not present on Kilauea samples that were kept in a freezer (Meeker et al. 2000; Meeker, personal communication 2000). The autoclave experiment described above, roughly simulating conditions for anhydrite within a pumice clast during airfall and after subaerial deposition and cooling, did not produce the observed surface features.

The anhydrite pyramids are in a class by themselves. They are uniform in morphology, composition, and size. The EBSD patterns suggest that the features grew epitaxially on the anhydrite phenocrysts (Figs. 1e and 1f). In addition, the pyramids have melt (bubble walls) frozen against them (Fig. 6), which is evidence for an origin at a temperature between the Pinatubo dacite solidus of ~700 °C (Scaillet and Evans 1999) and 780 °C.

**Fluid or melt origin for the pyramids?**

In the Mt. Pinatubo dacitic pumice, the level of S in the glass is low. Rutherford and Devine (1996) found that S in melt inclusions ranged from 55–77 ppm, whereas S in matrix glass was 19–40 ppm lower. Their experimental melt solubility study of the Pinatubo dacite, at near pre-eruptive conditions [~2000 bars ($P_{water} = P_{H_2O}$), ~800 °C and ~NNO + 3.5], showed that ~60 ± 20 ppm S could have been dissolved in the anhydrite-saturated melt. Anhydrite was therefore in equilibrium with the melt under these pre-eruptive conditions. Melt-anhydrite equilibrium does not preclude the pyramids from having precipitated from the melt prior to eruption. However, there is persuasive evidence that the pyramids likely resulted from precipitation of anhydrite from a supercritical H$_2$O-CO$_2$-SO$_2$ fluid upon pre-existing phenocrysts.

First, texturally the scattered surface pyramids represent a mode of crystal nucleation and growth distinct from the normal mode for crystal growth in the melt—that of attachment of atoms to surface ledge edges, with kink-attachments and lateral growth of the layer across the substrate surface (Tiller 1991).

Second, the distribution and morphology of the pyramids resembles “hillocks” observed during epitaxial growth of CdHgTe by chemical vapor deposition, CVD (C. Noble and J. Terlet, personal communication 2000), and of GaN grown by CVD. Figure 11 shows GaN pyramids grown by F. Dwikusuma at the Department of Chemical Engineering, University of Wisconsin-Madison. These GaN pyramids occurred when rapid growth (1 μm/min) was initiated in an experimental chamber.
where NH₃ and GaCl gas were reacting at 1100 °C and 1 bar. A slower growth rate (~1 μm/h) produced a smooth GaN layer. Published SEM images of similar features on a variety of substrates produced by CVD (e.g., Zheleva et al. 2001; Besmann et al. 1992) support this hypothesis.

The construction of a single hexagonal-shaped anhydrite pyramid from smaller (~100 nm) surface phases (Figs. 11e and 11f) may be explained by rapid anhydrite growth from four-sided pyramids whose bases grew together creating six-sided bases. This type of amalgamation process occurs in CVD (Figs. 11a–d).

Third, the SOLVGAS modeling shows that a high-temperature volcanic gas appropriate for Pinatubo could have been saturated with anhydrite at the estimated pre-eruptive temperature in the upper conduit at 500 bars pressure. The pressure constraint is not a physical limit to the process envisioned but is a limit on the calculation. As such, pre-existing anhydrite phenocrysts would have provided ideal nucleation sites.

Fourth, Pasteris et al. (1996) examined inclusions in phenocrysts, focusing on gas and liquid inclusions, and showed that an H₂O-CO₂-SO₂ fluid coexisted with the dacitic melt at depth. We postulate that this fluid may have been the source of the observed pyramids.

Thus, the evidence is consistent with a model where anhydrite phenocrysts provided substrates for nucleation and growth of anhydrite from a high-temperature vapor—a process we term magmatic vapor deposition, which is similar to the industrial process. The Ca mass-balance calculations indicate that there was sufficient Ca to cover some anhydrite phenocrysts with anhydrite pyramids, but that this occurred in only a small fraction of the erupted magma.

The limited extent of pyramidal nucleation and growth suggests that the deposition process may have been transient. Possible plagioclase growth rates and the extent of plagioclase growth trapping a pyramid-bearing anhydrite inclusion (Fig. 1c) provide evidence that some pyramids were deposited during the weeks to months prior to the major eruption (Fournelle, unpublished data). This would be consistent with pyramidal development having been triggered by eruptive events.

Mastin and Ghiorso (2001) present thermodynamic calculations indicating that constant entropy cooling in an explosive eruption of an evolved magma, at conditions similar to the pre-eruptive system at Mt. Pinatubo, could cause as much as 200 °C cooling. Their work suggests that isothermal conditions during eruption may not necessarily be a valid assumption. It is conceivable that this process could give rise to vapor precipitation of anhydrite (Fig. 10b). However, the actual pressure and temperature route traveled by the erupted products is constrained relatively poorly. The physical evidence, as collected from SEM images, suggests that at least a majority of the pyramids precipitated prior to eruption: anhydrite surface growths observed on an anhydrite inclusion, textural relations of pyramids walled-in by vesicular glass, and the lack of pyramidal surface growths inside vesicles.

**Anhydrite dissolution?**

Anhydrite breakdown in the conduit and eruption cloud has been discussed as a source for excess S vented to the atmosphere during the June 15, 1991 climactic eruption. The amount of SO₂ injected into the atmosphere contained about an order of magnitude more S than could have been dissolved in the volume of erupted silicate melt at the pre-eruption conditions (Gerlach et al. 1996). This observation led Westrich and Gerlach (1992) to hypothesize that most magmatic S had partitioned into a water-rich vapor phase at depth some time prior to eruption. A contradictory hypothesis was also developed by Ruth erford and Devine (1991, 1996) and Baker and Rutherford (1992), which stated that decomposition of anhydrite may have yielded the source of the excess S vented to the atmosphere. In addition, Kress (1997) proposed a model, mainly based on thermodynamic calculations, to explain how the source of the SO₂ could have been attributed to anhydrite decomposition as a result of mixing a sulfide-saturated basaltic magma into the oxidized, sulfate-saturated dacitic magma chamber.

Anhydrite dissolution could have occurred through interaction with a water-rich fluid, not the melt that had a small amount of S dissolved in it, close to the experimentally determined value for anhydrite saturation.

Fournelle et al. (1996) studied the effect of static distilled water upon anhydrite at room temperature, and observed crystallographically controlled etch pits forming after 2 months. The autoclave experiments discussed here, run for 240 to 280 min at 120 °C with both distilled as well as acidic water, yielded no observable surface features.

These experiments suggest that it was unlikely that etch pits observed on the anhydrite crystals (collected almost immediately after the eruption) were produced in the final stages of air fall and after deposition atop the roof in Angeles City, despite assumed brief contact with rainwater. It is unlikely that etch pits formed at room temperature in air-conditioned labs between 1991 and 1999 (no etch pits were observed on sedimentary anhydrite crushed and separated in 1992, stored under the same conditions as the Pinatubo anhydrite, and viewed in 1999).

The gas modeling suggests some possible conditions for anhydrite dissolution: lower Ca and/or lower SO₂ in the gas, lower fO₂, lower pressure or higher temperature, all would favor anhydrite dissolution. Gerlach et al. (1996) and Pasteris et al. (1996) concluded that an aqueous fluid phase had developed in the magma. Interaction of pre-existing phenocrysts with this fluid may have occurred some time before the June 15 climactic eruption. We suggest that anhydrite was precipitating out from the gas onto the {010} and {001} faces of pre-existing anhydrite phenocrysts at depth. When a conduit opened to the surface and pressure in the chamber dropped, the balance could have tipped away from precipitation, toward dissolution. This would explain not only the etch pits in the anhydrite phenocrysts, but also the craters (etch pits?) at the apices of the pyramids as well. The limited size and quantity of these pits and craters resulted from the short time available for the reactions to occur during the eruption. A drop of 250 bars, with the temperature remaining constant, would undersaturate the fluid with respect to anhydrite equivalent to a downward shift of the anhydrite saturation surface by 10−15 °C (i.e., log Q/K = −0.2, Fig. 10b).

We can estimate the magnitude of observed etch-pit formation, and therefore anhydrite phenocryst dissolution. SEM im-
**Figure 11.** Comparison of GaN (a–d, no tilt) and Pinatubo anhydrite pyramids (e–f, ~45° tilt). (a–d) SEM images of GaN pyramids grown atop sapphire at 1100 °C in 1 bar of NH₃ and GaCl, for 10 min. The substrate is smooth GaN grown slowly (~1 μm/h), whereas the pyramids result during rapid growth (1 μm/min). Courtesy of F. Dwikusuma, Department of Chemical Engineering, University of Wisconsin-Madison. The dark streaks in b are beam damage/contamination. Note how individual pyramids in c and d merge into a larger unit, similar to Pinatubo anhydrite pyramids e and f.
ages of phenocryst surfaces were used to estimate the appropriate surface areas. Pyramids account for roughly 30–50% of the surface area of most surfaces that have these features. Etch pits comprise roughly <1% to a maximum of 5% of the surface area.

Calculations suggest that the volume of anhydrite precipitated in the surface pyramids was from 15 to 350 times greater than the material removed in the etch pits. For the phenocrysts studied here, we see no evidence that dissolution of phenocryst anhydrite may have played a significant role in adding S to the vented gases. Rather, the anhydrite phenocrysts were apparently a sink for a small amount of the SO$_2$ in the vapor phase, precipitating as pyramids.

Sulfur, anhydrite and H$_2$O-CO$_2$ supercritical fluid in the Mt. Pinatubo magma

Ten years after the climactic eruption, the scientific community knows more about sulfur in the Pinatubo magma and the anhydrite present in the pumice. The evidence suggests that prior to the eruption, most of the S released as 20 Mt of SO$_2$ was distributed in a vapor phase at depth: the distribution coefficient of S (wt%) in vapor relative to S in melt was between 720 (Gerlach et al. 1996) and 950 (Wallace 2000). The Pinatubo magma clearly was heterogeneous in its anhydrite distribution, as evident by the lack of anhydrite inclusions observed in phenocrysts studied by Pasteris et al. (1996), vs. the abundance found by Fournelle et al. (1996). Presumably this difference represents heterogeneity of the magma body, which is also evident in the variability of S contents (~300 to ~2800 ppm) in the bulk pumice analyses reported in *Fire and Mud* (Newhall and Punongbayan 1996). This is not surprising as various levels of a long-lived magmatic system were erupted. It is also conceivable that at least some of the variability in S contents in the bulk pumices could be attributed to post-eruptive dissolution by meteoric and surface waters.

The existence of magmatic vapor deposition features, the anhydrite pyramids, is evidence that S first partitioned into the fluid phase at depth, and later was precipitating as anhydrite onto pre-existing phases, quite rapidly, at some point prior to the quenching of the melt. Here we have shown that anhydrite was a substrate, and earlier work (Fournelle et al. 1996) suggested plagioclase was a substrate. It is also possible that a small amount of anhydrite could precipitate from the vapor phase onto phenocryst substrates—perhaps in a short interval prior to the eruption—then it also be possible that some of the anhydrite phenocrysts may have grown from the vapor, as suggested by Pallister et al. (1996)? Perhaps. The strong evidence for magmatic vapor deposition of anhydrite pyramids indicates that the conditions at depth were favorable. The mass-balance calculations suggest that the Ca content of the vapor would have been a limiting factor. What conditions would favor more volumetric saturation of anhydrite phenocrysts? There are at least two possibilities: (1) the vapor would have to be supersaturated with respect to Ca and undersaturated with respect to Si and Al, to preclude silicate phases apportioning the Ca; and (2) there could be a heterogeneous reaction of the vapor with other Ca-bearing phases, such as plagioclase and/or apatite. This topic warrants further study and may be resolved with modeling or possibly oxygen isotope analysis.

The intimate association of apatite with anhydrite (Fig. 1) is a curious occurrence, previously recognized, but unexplained. We speculate that apatite also may have been precipitating from the vapor. SOLV GAS does not have thermodynamic data for P and therefore cannot currently be used to evaluate this possibility.

ACKNOWLEDGMENTS

R.J. acknowledges Senior Thesis funding from the Albert and Alice Weeks Fund of the Department of Geology and Geophysics, University of Wisconsin-Madison, and encouragement from William Peck. J.F. acknowledges the postdoctoral experience with Bill Melson at the Department Mineral Sciences, Smithsonian Institution (and Bill’s excitement in finding anhydrite in Nevada del Ruiz pumice), and Bruce Marsh for support during initial stages of this work at Johns Hopkins University. S.W. acknowledges support from NSF (EAR 9706382) and DOE (93ER14329). We thank Rick Noll for assistance with the LEO SEM work, and Mark Reed for supplying the gas modeling software. The manuscript greatly benefited from reviews by Terrance Gerlach, James Luhr, John Pallister, Bernard Evans, Malcom Rutherford, Ilya Bindeman, and Brad Singer. Comments from Mark Reed and Jill Banfield were helpful.

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