Decay-induced biomineralization of the saguaro cactus (*Carnegiea gigantea*)

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ABSTRACT

The saguaro, *Carnegiea gigantea* (Englemann), is a columnar cactus that grows to 15 m tall and weighs up to several tons, of which 85 to 90% of the mass is water. Roughly 18% of the dry mass consists of the biomineral weddellite ($CaC_2O_4 \cdot 2H_2O$). The C in the weddellite derives from atmospheric CO_2 via photosynthesis. A mature saguaro can contain on the order of 1×10^5 g of weddellite. The weddellite crystals occur as aggregates up to 1 mm wide. After the death of the saguaro, a series of minerals crystallize in the rotting flesh. These minerals form from elements released from the decay of the cactus by microorganisms and thus is a type of biologically induced mineralization. During the initial stages of decay, authigenic Mg- and Ca-bearing minerals crystallize from elements released by the putrefying flesh and include lansfordite ($MgCO_3 \cdot 5H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$), several polymorphs of $MgC_2O_4 \cdot 2H_2O$ including glushinskite, monohydrocalcite ($CaCO_3 \cdot H_2O$), calcite, vaterite, and several unidentified Mg-bearing phases. As the saguaro decays, the soft, water-rich pith shrinks, but the ribs and skin remain intact, producing warm, moist pockets within the dead saguaro. Abundant, glassy lansfordite crystals to 1 mm in diameter grow in these pockets during the cooler winter months. Further decay leaves a dried hollow shell covered by the saguaro skin, inside of which nesquehonite and monohydrocalcite crystallize. Lansfordite and nesquehonite are unstable in the desert and rapidly amorphize after exposure to the atmosphere. Magnesium oxalates are locally abundant in the decayed flesh and occur as crystals up to 1.5 mm in length. The common occurrence of fungal hyphae on the glushinskite suggests that it forms as a result of the reaction between oxalic acid released by fungi and the Mg-rich solutions of the rotting saguaro. During the final stages of decay, the pith consists of a pale-brown to tan-colored sand of weddellite and its transformation product monohydrocalcite. This sand lithifies to porous sponge-like masses during the final stages of saguaro decay. This monohydrocalcite further alters to calcite. The $\delta^{13}C_{VPDB}$ of the monohydrocalcite and calcite after weddellite range from -1.65 to $+0.76‰$. The calcite is subsequently solubilized and remobilized, precipitating as caliche in the desert soil, or redistributed by wind. In arid environments, the desert fauna metabolize the atmospheric C bound in the organic matter to CO_2. In contrast, decay of the saguaro adds atmospheric C to the soil as inorganic C via the transformation of the biomineral weddellite to calcite. In areas with high saguaro density, it is estimated that up to 2.4 $g/m^2/yr$ of calcite can be added to the desert from the decayed cacti. This inorganic C has geologically long soil residence times, thus effectively sequestering the atmospheric C.

INTRODUCTION

Decay affords an environment for authigenic minerals to crystallize. Under favorable conditions, these minerals, such as Ca phosphates and carbonates, can form in a matter of days or weeks and preserve labile tissues such as muscles (Briggs and Kear 1993; Sagemann et al. 1999). Microbial activity is both the driving force behind the decay and concomitant mineralization of soft tissues, and hence is a form of biologically induced mineralization (Lowenstam 1981).

Plant decay under aerobic conditions is a transformation process, with the aid of soil flora and fauna, into the compounds from which the plant was originally composed, predominantly CO_2 and water. In addition to C, H, and O, plants also contain significant quantities of essential macro-elements, such as Ca, Mg, K, and P (Ramirez et al. 2001). After death, these elements do not normally accumulate and crystallize within the decaying plants, although under certain circumstances, these

elements can be concentrated. For example, fungi actively concentrate Ca, Mg, and Fe in decaying wood and frequently produce insoluble Ca oxalates (Jellison et al. 1997 and references therein). In arid environments there is a lack of significant organic matter accumulation in soils, which reflects the efficiency of the combined abiotic and biotic decomposition processes (Whitford 1996; Murphy et al. 1998; Núñez et al. 2001).

The most common biominerals in plants are the oxalates weddellite ($CaC_2O_4 \cdot 2H_2O$) and whewellite ($CaC_2O_4 \cdot H_2O$) (Franceschi and Horner 1980; Horner and Wagner 1995; Prychid and Rudall 1999). Their presence has been attributed to one or more of the following: detoxification, protection, structural strength, Ca storage, and light gathering and reflection (Horner and Wagner 1995; Volk et al. 2002). The C source for the oxalate in the Ca oxalates is atmospheric CO_2 (Kostman et al. 2001; Franceschi pers com). Calcium oxalates also occur in surficial, diagenetic, and hydrothermal deposits (Russ et al. 1996; Hofmann and Bernasconi 1998), and in meteorites (Fuchs et al. 1973). In addition, Ca oxalate is widely recognized be-

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cause of its common association with kidney stone disease (Milliner 1995).

Anatomical investigations reveal Ca oxalates in the majority of cacti (Bailey 1961; Anderson and Boke 1969; Conde 1975; Anderson and Skillman 1984; Mauseth 1996; Porembski 1996; Mauseth et al. 1998). Recent systematic work has demonstrated the chemotaxanomic value of Ca oxalates, with taxa of the Opuntioideae subfamily containing whewellite, and species from the Ceroideae subfamily containing weddellite (Monje and Baran 2002). Weddellite or whewellite can constitute up to 85% of the dry organic matter of cacti (Chevain 1938), although <50% dry weight is more normal (Rivera and Smith 1979).

In addition to the Ca oxalates, a host of minerals occur in plants including calcite, Mg oxalate, sylvite, various forms of crystalline and amorphous SiO_2, barite, and $CaSO_4$ (Cowgill 1989; Wu and Kuo-Huang 1997; Monje and Baran 2000; Pritchard et al. 2000), and a range of Fe-rich biominerals including magnetite, ε-Fe_2O_3, and hematite (Gajdardziska-Josifovska et al. 2001; McClean et al. 2001). Despite this mineral diversity, few plants release or concentrate significant quantities of biominerals after their death. One notable exception are silica phytoliths, which can accumulate in soils and provide important palaeoenvironmental information (e.g., Piperno 1988).

Here we report on the decay of the saguaro, which affords an environment for a series of minerals to crystallize that are either rare or not normally found in hot deserts. Considering the potential for large quantities of Ca oxalates to be released as a result of plant decay, it is surprising that little is known about their breakdown in the environment. Understanding this breakdown provides insights into Ca and oxalate cycling and their roles in soil genesis and fertility.

MATERIALS AND METHODS

Sample collection and Ca oxalate extraction

Samples of recently fallen, decaying, and decayed saguaro, (*Carnegiea gigantea* Engelmann), were collected at various sites throughout south and west central Arizona. Weddellite was extracted from a living saguaro that had been blown over by a storm (the saguaro pieces were kindly supplied from a legally salvaged native saguaro by Arizona Cactus Sales, Chandler, Arizona). Several slices were taken from the fallen saguaro. Weddellite was extracted by first drying the saguaro slices in an oven at 60 °C, and then dissolving the organic matter in a vat of dilute sodium hypochlorite (bleach) at room temperature. The weddellite remained as an insoluble sediment.

Analytical methods

Minerals were identified by powder x-ray diffractometry (XRD), scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS), and optical microscopy. The EDS data was used to confirm the identity of the major cations in the minerals and thus to help corroborate the powder XRD identifications. Isotopic analyses were performed using the method of McCrea (1950). Analytical uncertainties for $\delta^{13}C_{VPDB}$ (Vienna Peedee belemnite) and $\delta^{18}O_{VSMOW}$ are ±0.1 and ±0.2 ‰, respectively, where $\delta^{18}O_{VSMOW} = 1.0309$ and $\delta^{13}C_{VPDB} = +30.9$. Samples for isotopic analyses were acquired in the vicinity of the South Maricopa Mountain Wilderness east of Gila Bend, Arizona.

RESULTS AND DISCUSSION

Introduction

The saguaro is a columnar cactus endemic to the Sonoran desert, grows to 15 m high, can weigh more than several tons

of which 85 to 95% of the mass is water, and live for 200 years or more (Figs. 1a and 1b). Dried saguaro flesh contains the following average major nutrient and cation compositions: 17.99 mg/g Mg, 77.37 mg/g Ca, 0.5 mg/g Na, 7.04 mg/g K, 0.45 mg/g P, and 11.47 mg/g N (Kolberg and Lajtha 1997). Calcium concentrations in saguaros exhibit large variations over sites in the Sonoran desert ranging from 32.95 to 145.18 mg/g. In cacti, a significant proportion of the Ca resides in Ca oxalates, although mucilage, which is common in the saguaro, also contains abundant Ca (Trachtenberg and Mayer 1982). The Ca and Mg contents of cacti are significantly higher than those of leafy vascular plants of semiarid regions of North America (Ramirez et al. 2001).

Weddellite in the saguaro

Abundant quantities of weddellite were found throughout the saguaro stem and roots. The crystals typically occur as druses (Fig. 1c) up to 1 mm in diameter, with differences in their shape depending on location within the cactus. Druses in the pith are normally rounded in cross section with few sharp projections, whereas crystal "sand" is common within and around the secondary xylem (woody ribs). The largest crystals occur in the cortex between the secondary xylem and the tough outer skin. No other biominerals were found in the living saguaro.

A total of 2.2 kg of dried saguaro contained 371.6 g of weddellite, which is equivalent to ca. 3.1 kg weddellite per meter of stem. The weddellite quantity is equivalent to 18 dry
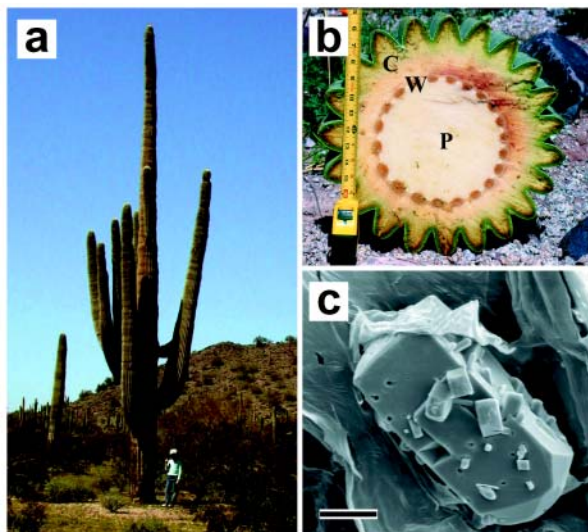
FIGURE 1. (**a**) A large multibranched saguaro of height 10.5 m and total stem length of 39.4 m. This saguaro contains an estimated 1.2×10^5 g of weddellite. The young girl is 125 cm tall. (**b**) Cross section of a saguaro stem. P = pith, W = woody ribs (secondary xylem), and C = cortex. Tape measure in inches. (**c**) Scanning electron micrograph of a typical weddellite cluster partially embedded in the saguaro matrix. The weddellite cluster exhibits a large euhedral crystal dominated by the {100} prism. Only one side of the tetragonal bipyramid has formed. The ends of the {100} prism show the {001} pinacoid. Scale bar in **c** equals 150 µm.

wt%, corresponding to 46 mg/g Ca of dried saguaro. This Ca content is consistent with previous studies showing between 33 and 145 mg/g Ca for saguaros (Kolberg and Lajtha 1997). Considering the large sizes of saguaros, they contain significant quantities of weddellite. For example, the saguaro shown in Figure 1a contains an estimated 1.2×10^5 g of weddellite.

Saguaro decay and biomineralization

The onset of saguaro death is visible as a black rot exudate streaming down the surface of the cactus and pooling on the desert floor. This stage of saguaro death has been studied extensively because of the cactus-yeast-*Drosophilia* model ecological system (Barker and Starmer 1982). The rotting tissue is a haven for life in an otherwise arid environment, providing a wet organic soup for a multitude of organisms (Starmer et al. 1981; Foster and Fogleman 1993; Castrezana and Markow 2001). Decay of the saguaro affords an environment for a series of minerals to crystallize that are either rare or not normally found in hot arid environments. The saguaro decay can be divided into six stages based on visual characteristics and mineralogy.

(1) The flesh of the saguaro is black and infected by yeasts and bacteria and colonized by numerous insects. A black liquid drips from cracks in the skin. The water-storage and muci-lage cells of the pith and cortex shrink leaving a lattice network of cortical bundles. The soft, water-rich pith reduces in volume as it rots and dehydrates but the ribs and skin remain intact, producing warm (up to 50 °C) moist pockets within the dead saguaro. Nine minerals are found within the pockets: weddellite, several polytypes of $MgC_2O_4 \cdot 2H_2O$ (the β-form is called glushinskite), lansfordite ($MgCO_3 \cdot 5H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$), monohydrocalcite ($CaCO_3 \cdot H_2O$), two unidentified Mg-C-O-H-bearing minerals, and rare vaterite and calcite.

(2) The saguaro skin is brown, and the wet organic matter has dried. The outer skin is still intact but begins to crack. Lansfordite is no longer present but nesquehonite and monohydrocalcite are common within the protected saguaro and form tan-colored coatings.

(3) The skin cracks and flakes away from the ribs and in cross section the saguaro is elliptical. Most nesquehonite and glushinskite has altered to a white x-ray amorphous powder. As more organic matter decomposes, the weddellite increases as a proportion of the decomposing saguaro. Weddellite is concentrated as a layer on the bottom of the pith. Weddellite begins to transform to monohydrocalcite.

(4) Only a little skin remains attached to the ribs. The former pith area is composed of a pale brown to tan-colored "sand" of
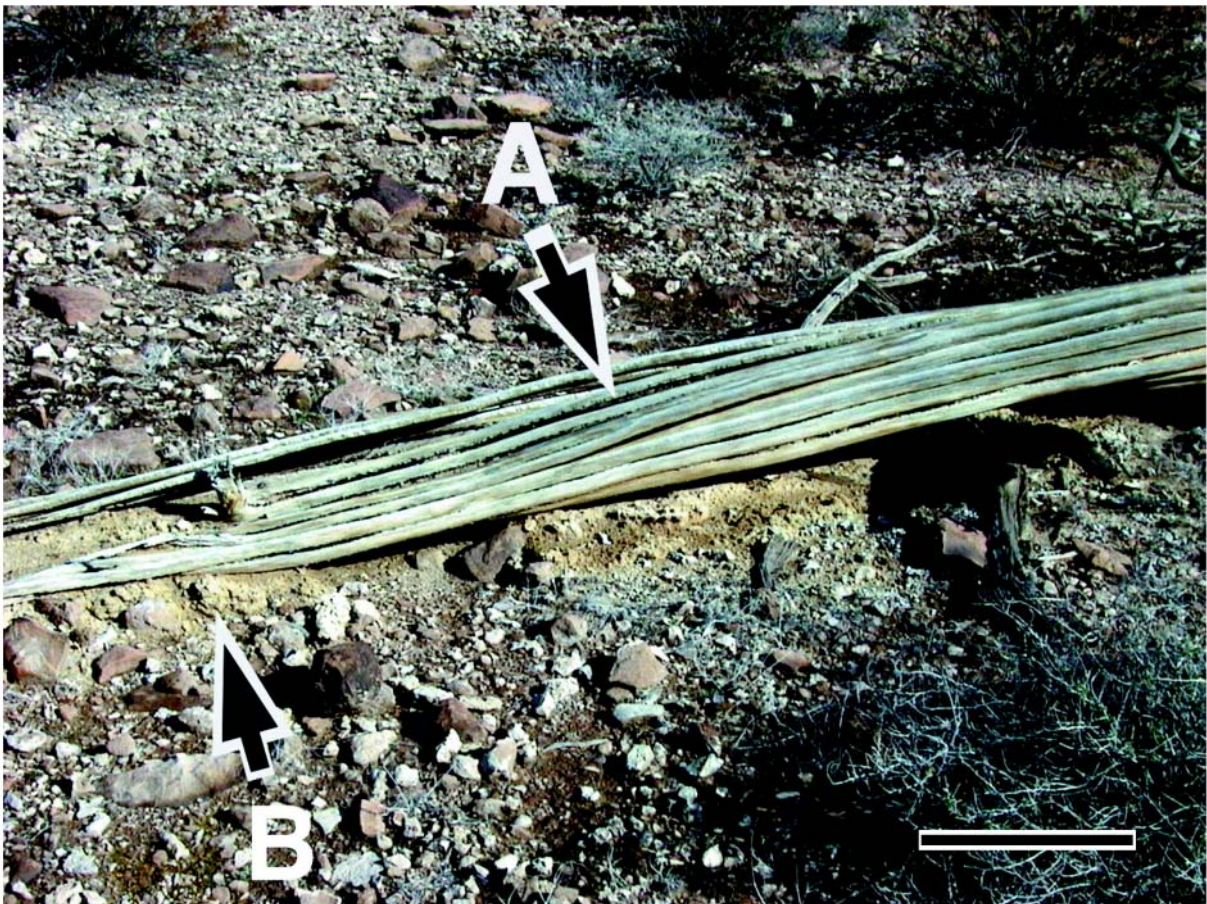

FIGURE 2. Photograph of a decayed saguaro showing the woody ribs (**A**) and the tan-colored monohydrocalcite (**B**) spilling onto the desert floor. The woody ribs are the support mechanism for the saguaro. Note the white pieces of caliche littering the desert floor. Scale bar = 0.5 m.

weddellite and monohydrocalcite (Fig. 2). This sand lithifies to porous sponge-like masses of monohydrocalcite.

(5) Little remains of the saguaro and most ribs and skin have decomposed. The majority of the weddellite has altered to monohydrocalcite, which begins to transform to calcite.

(6) Lumps of porous calcite with minor monohydrocalcite remain on the desert floor.

Mineralogy of the decaying saguaro

Magnesium-bearing minerals. The source of Mg in the decaying saguaro is the putrefying cactus flesh. Magnesium is an essential element for plant growth and the ubiquity of the Mg-bearing minerals reflects the high Mg content of the saguaro tissues, which is between 1 and 2 wt% (Kolberg and Lajtha 1997). The Mg-bearing minerals are not present in the living cactus and crystallize as a result of the microenvironment afforded by the decay. These minerals are highly unstable in the dry desert atmosphere and lansfordite becomes x-ray amorphous within a few hours when left uncovered and nesquehonite over periods of a few days or weeks.

Nesquehonite is the most common Mg-bearing mineral in the decayed saguaro. It occurs in several distinct forms: brown microcrystalline coatings on the organic tissue, tan botryoidal masses up to 0.5 mm thick, crystalline sugary coatings, thin coatings with a silky luster, and as single euhedral crystals. The SEM (Fig. 3) and optical microscope reveal three distinct morphologies: lath-like prisms, stubby euhedral crystals, and plates to 1 mm wide. Consistent with previous studies (Giester et al. 2000), these crystals commonly exhibit a pseudo-orthorhombic morphology. The elongate habit is characteristic of synthetic (Ming and Franklin 1985) and natural (Kiss and Jánosi 1993) materials. The brown to tan coloration is likely caused by organic impurities. Chemical analysis by SEM-EDS showed Mg to be the only detectable metal cation. Fungal hyphae are commonly draped over the nesquehonite (Fig. 3b).

Nesquehonite has received much attention because it is a common weathering product of Antarctic meteorites (Tull et al. 1988; Velbel et al. 1991). It also occurs in caves (Fischbeck and Müller 1971), as a recent efflorescence in mines, and crack fillings from epihydrothermal waters (Kiss and Jánosi 1993). Nesquehonite precipitates in HCO_3^--bearing solutions containing Mg (Ming and Franklin 1985; Liu et al. 1990). The nesquehonite in the saguaro crystallizes in an environment that is saturated in moisture and enriched in CO_2 from the decay according to:

$$Mg^{2+} + 2HCO_3^- + 2H_2O \rightarrow MgCO_3 \cdot 3H_2O + CO_2 \qquad (1)$$

where the bicarbonate anion is produced by the moisture and CO_2-enriched atmosphere. The CO_2 enrichment is derived from the microbial decomposition of the organic matter.

Lansfordite was found in a single decaying saguaro, which still had an abundance of putrefying matter. Samples were collected during the winter of 2001, with average low and high temperatures for January 2001 of 4.1 and 20.3 °C, respectively (www.worldclimate.com). Subsequent collections from decaying saguaros during the summer failed to reveal lansfordite, when temperatures can reach above 50 °C in the shade. These observations suggest that lansfordite formed after the 2000 sum-
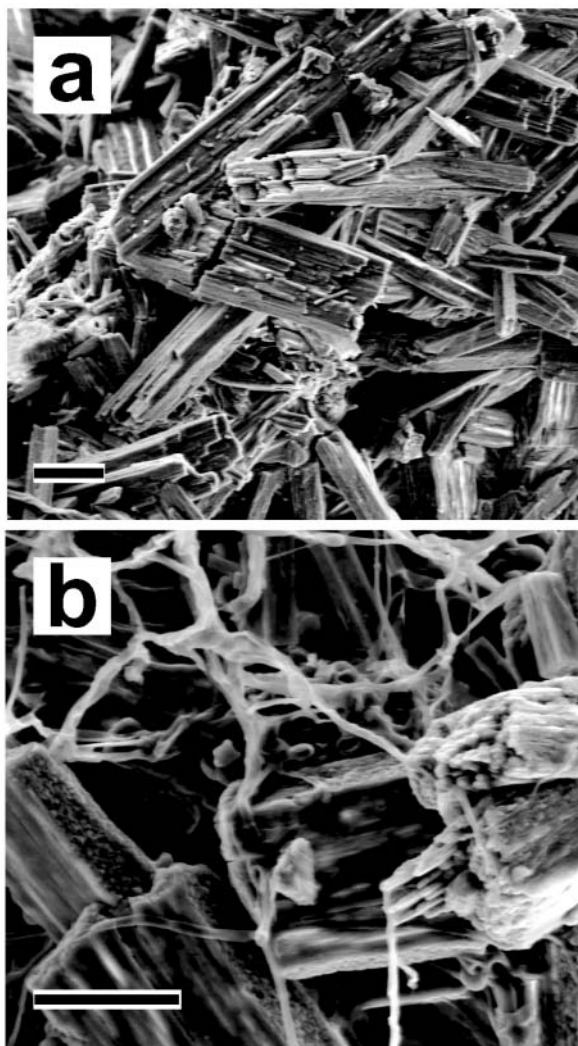
FIGURE 3. Scanning electron micrographs of nesquehonite clusters. (**a**) typical elongated habit, and (**b**) stubby crystals draped with fungal hyphae. Scale bars = 50 µm.

mer period, and would undoubtedly have decomposed before summer 2001. The geological rarity of lansfordite is partly dictated by its tendency to dehydrate under ambient conditions.
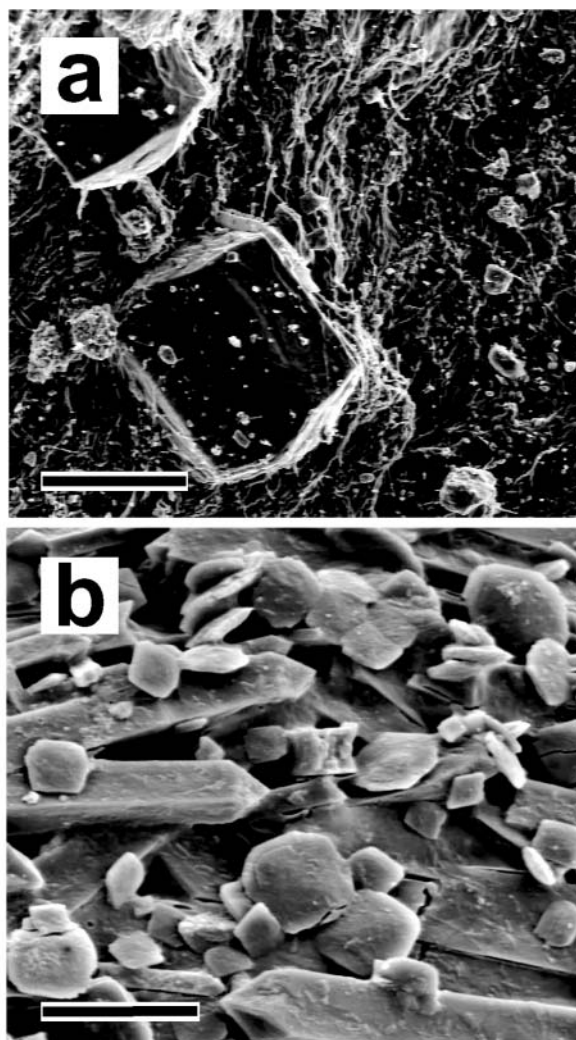
Lansfordite occurs as euhedral, glassy, tabular to short prismatic, single crystals and clusters up to 1 mm in diameter (Fig. 4). Samples are monomineralic and free of nesquehonite and monohydrocalcite. The crystals readily become opaque and white when exposed to air at room temperature. The dehydrated lansfordite is x-ray amorphous, without nesquehonite reflections. Presumably, lansfordite formed by a similar reaction as for nesquehonite, but at relatively low temperatures and high CO_2 saturation and moisture levels. Ming and Franklin (1985) and Liu et al. (1990) synthesized lansfordite by passing CO_2 through an MgO-H_2O slurry. The experiments of Ming and Franklin (1985) show that synthesis of pure lansfordite free of nesquehonite requires low temperatures, <10 °C, and P_{CO_2} of $>10^{-4.5}$ MPa.
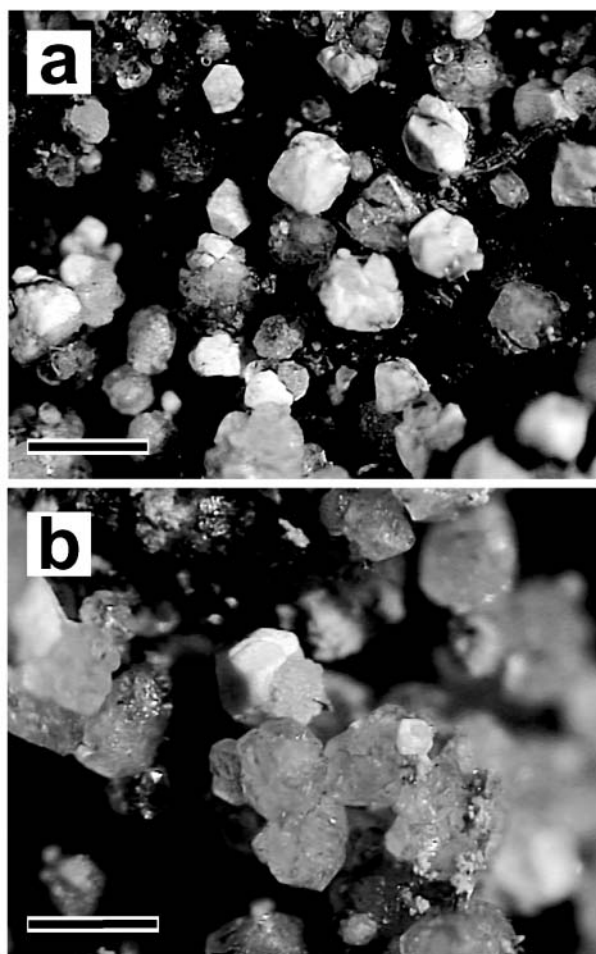
FIGURE 4. Optical images of lansfordite. (**a**) glassy and opaque white (dehydrated) crystals on black saguaro matrix. (**b**) clusters of glassy crystals and one dehydrated crystal The euhedral nature of the lansfordite is more easily seen on the white crystal. Scale bars = 800 µm.

FIGURE 5. Scanning electron micrographs of glushinskite. (**a**) Two large euhedral crystals partially embedded in the dried, rotten saguaro matrix. (**b**) Small plate-like glushinskite crystals adhering to weddellite needles. Scale bar in **a** equals 150 µm and **b** equals 20 µm.

The powder XRD patterns of some samples of Mg oxalate from the decaying saguaro exhibit reflections that are identical to that of glushinskite, PDF 28-625, although selected samples contained crystals that exhibit additional reflections. These extra reflections arise from stacking disorder along (001), which results in a series of well-ordered structures, i.e., glushinskite, and a range of less well-ordered phases (Dubernat and Pezerat 1974). This stacking gives rise to a series of polytypes, although only glushinskite has been described and approved as a mineral. Therefore, for simplicity, all the Mg oxalates in the rotten saguaro are referred to as glushinskite.

Glushinskite is locally abundant in the rotten saguaro flesh, but not in the living cactus. The crystals are euhedral, glassy, to 1.5 mm long, and exhibit forms of the hexagonal and orthorhombic systems (Fig. 5), despite their monoclinic symmetry (Levy et al. 1971). Three forms are dominant: rhombohedra, hexagonal prisms, and a combination of a rhombic prism and rhombic dipyramid. The common occurrence of fungal hyphae on glushinskite suggests that it forms as a result of the reaction between oxalic acid, released by fungi, and Mg-rich solutions

of the rotting saguaro. Oxalic acid is often produced in large quantities by wood-decaying fungi (Jellison et al. 1997). Terrestrial magnesium oxalates are normally associated with biological activity such as lesions on coffee leaves (Rao and Tewari 1989), reaction of oxalic acid secreted by lichens with Mg-rich rocks (Wilson et al. 1980), and in plants of arid regions (Cowgill 1989).

Two unidentified Mg-bearing minerals are locally common within the vascular tissues surrounding the woody ribs of the rotten saguaro. These tissues are responsible for the storage and transport of sugars and other organic compounds to the rest of the plant. Both minerals are crystalline as determined by powder XRD, occur as hemispherical or lenticular aggregates, with Mg as the only metal detectable by SEM-EDS. The first mineral is clear to opaque and cannot be matched with the patterns in the PDF database. The second mineral is white and powdery and appears to be an alteration product of the first mineral. Its XRD pattern matches a mixture of Mg oxide ac-
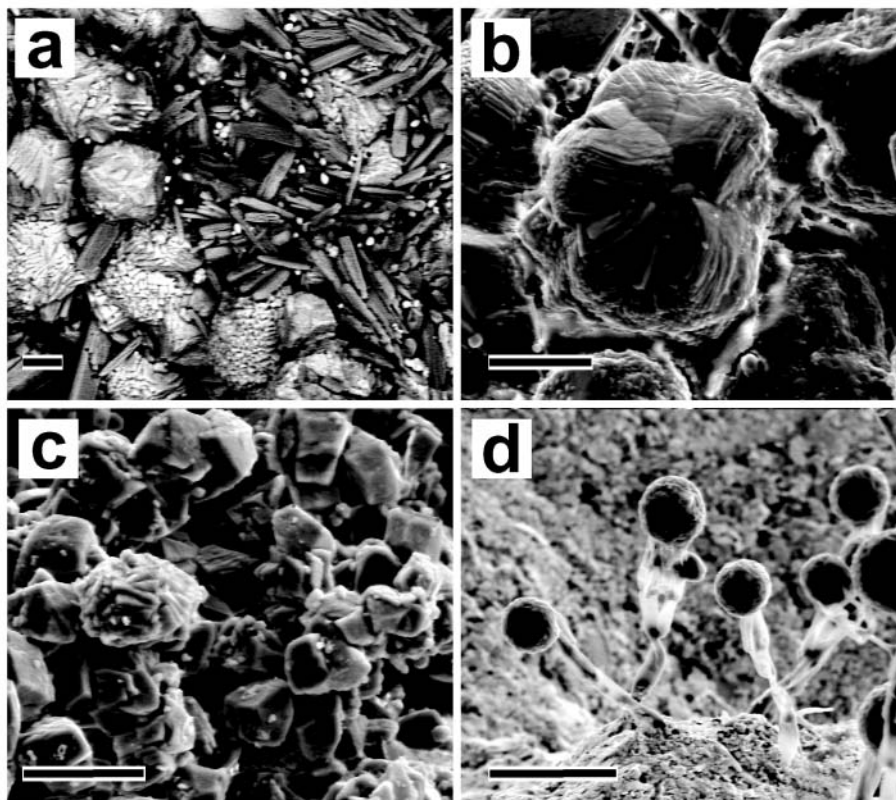
FIGURE 6. Scanning electron micrographs of monohydrocalcite from the rotten saguaro. (**a**) Backscattered electron image of monohydrocalcite (bright) and nesquehonite (darker needles). (**b**) Secondary electron image of one of the rounded, multiply twinned monohydrocalcite clusters. (**c**) Euhedral single crystals of monohydrocalcite exhibiting the trigonal pyramidal habit. (**d**) Fruiting bodies of fungal hyphae (sporangia) on monohydrocalcite. The spherical fruiting bodies are composed predominantly of C, O, Mg, and Ca. Scale bars = 40 μm.

etate hydrate ($C_{24}H_{36}Mg_7O_{25} \cdot 8H_2O$ – PDF 14-0823) and Mg hydrogen malonate hydrate ($C_6H_6MgO_8 \cdot 2H_2O$ – PDF 24-1794).

Calcium-bearing minerals. Monohydrocalcite is locally abundant within the damp lattice network of the pith and cortex beneath the protective skin. It is not found in direct contact with the wet decaying matter. The mineral occurs as tan-colored coatings and single and multiply twinned crystals up to <100 μm in diameter (Figs. 6a, 6b, and 6c). Crystals that exhibit faces with a trigonal pyramidal habit are common (Fig. 6c). The saguaro-derived crystals have similar shapes and sizes to those from African lake sediments (Stoffers and Fischbeck 1974).

A common factor in several of the syntheses and natural occurrences of monohydrocalcite is the presence of Mg, which inhibits the growth of calcite (Taylor 1975 and references therein). For example, the monohydrocalcite in speleothems is thought to have formed when Mg-bearing carbonate solutions that sprayed onto cave walls evaporated (Fischbeck and Müller 1971; Fischbeck 1976). Similarly, synthetic monohydrocalcite from air scrubbers of air-conditioning plants (Marschner 1969) is deposited above the water surface in the spray zone, whereas carbonate coatings that formed in the same chamber but under water consisted of calcite. Marschner further describes the common occurrence of synthetic nesquehonite with the monohydrocalcite.

The Ca for the monohydrocalcite in the decaying saguaro is derived from the putrefying cactus flesh. One prominent source of Ca in cacti is mucilage, which is a fibrous polysaccharide (Gibson and Nobel 1990). Mucilage can contain up to 20% of the insoluble Ca (Gibson and Nobel 1990). Weddellite is stable during

TABLE 1. Comparison of isotopic data for carbonates formed in the decayed saguaro with selected carbonates formed in the saguaro environment

Mineral	$^{13}C_{pdb}$	$^{18}O_{pdb}$	$^{18}O_{SMOW}$
Weddellite from cacti*	ca. –8	–	–
MHC† and minor nesquehonite	–3.97	–0.83	30.00
MHC after weddellite	0.76	0.07	30.93
MHC after weddellite	–0.87	–1.00	29.83
Calcite after MHC after weddellite	–1.65	–0.34	30.51
Pavement calcite‡	4.34	–2.25	28.5
Caliche§	–4.2 to 0.7	–6.1 to –3.2	24.5 to 25.6

* Weddellite data from Rivera and Smith 1979.
† MHC = monohydrocalcite.
‡ Pavement calcite formed as a result of Phoenix municipal water that collected and then evaporated on concrete sidewalks over a period of several years.
§ Caliche samples are from the South Maricopa Mountain Wilderness.

the initial stages of decay and so is not a source of soluble Ca.

Stable-isotope data provide evidence that organic C from the decaying saguaro is the source of the C in the monohydrocalcite. The monohydrocalcite is depleted in ^{13}C relative to ^{12}C (Table 1), which is indicative of a light C source derived from the cactus tissues. Tissues of cacti have $\delta^{13}C$ values of between –10.5 and –14.1‰ (Rivera and Smith 1979;

van de Water 2002), consistent with plants that metabolize CO_2 via the Crassulacean Acid Metabolism (CAM) route. Using the recently published C-isotope fractionation factor ($10^3 \ln\alpha$) of 8.35‰ for monohydrocalcite – $CO_{2(g)}$ (Jiménez-López et al. 2001) and an average $\delta^{13}C$ for cactus tissue of –12‰, we would expect the monohydrocalcite to have a $\delta^{13}C$ value of –3.65‰. This predicted value is close to the measured value (Table 1) and indicates two points. First, the system is closed during the monohydrocalcite precipitation. If the system had been open to the atmosphere then there would have been mixing with the atmospheric CO_2 producing $\delta^{13}C$ values of between –3.65 and +1.35 ‰. Second, the $\delta^{13}C$ of the decaying saguaro and the CO_2 respired by the heterotrophic microorganisms are similar, consistent with previous studies that showed that the $\delta^{13}C$ of CO_2 respired from soils by microorganisms decomposing plant matter is nearly the same as the flora at the site (Cerling et al. 1991).

Aside from the ubiquitous, unaltered weddellite, the only other Ca-bearing minerals identified were rare calcite and vaterite. These minerals were only encountered in one saguaro as a white, powdery coating, together with nesquehonite and glushinskite.

Weddellite transformation

It is not until the majority of the organic matter and Mg-bearing minerals have decomposed that weddellite transforms to monohydrocalcite. In hand specimen, the bulk monohydrocalcite is light-weight, friable, porous, tan colored, and forms individual masses up to 20 cm across and 5 cm thick (Fig. 7). Under the optical microscope, the samples reveal agglomerated hollow spheres some with a core of relict weddellite (Figs. 8a, 8b, and 8c). The weddellite at the center of the monohydrocalcite shows abundant evidence of dissolution in the form of bowl-shaped etch pits. The etched weddellite is covered in ca. 5 μm sized, rugby-ball-shaped crystallites of monohydrocalcite (Fig. 8d). These crystallites fuse together to form the monohydrocalcite shells.

The stability of weddellite under dry conditions in the Sonoran desert is revealed by a series of ongoing experiments

FIGURE 7. Photograph of a deposit of calcite and monohydrocalcite after weddellite. Note the characteristic tan color of the material and the absence of the decayed saguaro. Also visible are pieces of caliche on the desert floor.
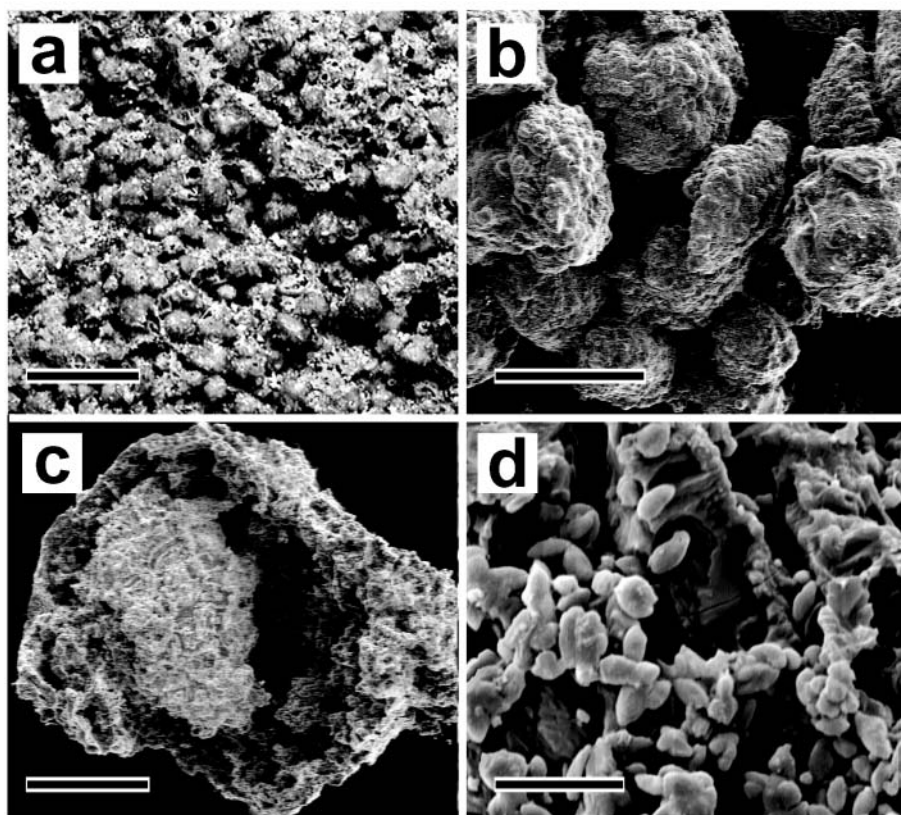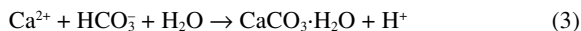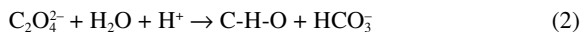

FIGURE 8. Monohydrocalcite after weddellite formed in the later stages of saguaro decay. (a) Optical image showing the high porosity and rounded particles. (b) SEM image of (a). (c) Inside one monohydrocalcite sphere revealing the relict weddellite core (light-colored patch). (d) Small, rugby-ball-shaped monohydrocalcite crystallites on corroded weddellite. Scale bar in a equals 4 mm, in b 400 μm, c 100 μm, and d 30 μm.

(Garvie, unpublished data). These experiments comprise several grams of saguaro-derived weddellite enclosed in porous nylon bags placed on the desert floor. After ca. 2 years, there is no evidence of dissolution or alteration of the weddellite. These two years were exceptionally dry with rainfalls of <5 cm per annum. Another bag of weddellite was placed on a dark varnish-covered rock where surface temperatures regularly exceed 70 °C in the summer. Again, the weddellite remained unaltered over the two year period. These data suggest that saguaro-derived weddellite is chemically stable under dry, hot, essentially abiotic conditions.

In contrast, the weddellite in the decayed saguaro transforms to monohydrocalcite over a period of a few years. Although the transformation mechanism is not fully understood, it is suggested that bacteria play a central role in the damp and warm conditions of the decaying saguaro. Evidence for this interpretation is twofold. First, microbes able to attack oxalates are widely distributed in natural ecosystems (Allison et al. 1995). Second, the monohydrocalcite is enriched in ^{13}C relative to the oxalate: δ^{13}C = $-8‰$ for weddellite to values between -0.87 and $+0.76‰$ for the monohydrocalcite (Table 1). This enrichment may be explained by bacterial decomposition of the oxalate into light CO_2 leaving heavy residual ^{13}C for the monohydrocalcite, suggesting a new biologically induced mineral-transformation mechanism. This transformation is generalized as:

$$C_2O_4^{2-} + H_2O + H^+ \rightarrow C\text{-}H\text{-}O + HCO_3^- \qquad (2)$$

$$Ca^{2+} + HCO_3^- + H_2O \rightarrow CaCO_3 \cdot H_2O + H^+ \qquad (3)$$

In Reaction 2, the oxalate is catabolized by the microorganisms into an organic component, C-H-O, which is utilized by the microbe, and an inorganic part. Monohydrocalcite forms from the released bicarbonate in the presence of water. Reaction 3 may also be mediated by microorganisms, as they have been implicated in the precipitation of monohydrocalcite (Rivadeneyra et al. 1997; Jones et al. 1999).

The longevity of the monohydrocalcite likely benefits from the aridity of the Sonoran desert. Laboratory experiments illustrate the stability of monohydrocalcite under dry conditions to at least 120 °C (Stoffers and Fischbeck 1974) and 100 °C for 18 days (Marschner 1969). Under pure water, monohydrocalcite is rapidly transformed into aragonite (Marschner 1969) or calcite (Stoffers and Fischbeck 1974). Additives may either accelerate or impede this transformation. For example, <0.1 mol% of $MgCl_2$ in the water entirely prevents monohydrocalcite transformation (Marschner 1969). Thus, the data reveal the stability of monohydrocalcite in the presence of Mg and under dry conditions.

The monohydrocalcite gradually transforms over a few years into calcite. Hand samples that are predominantly calcite still exhibit the same porous texture characteristic of the monohydrocalcite. The isotopic data reveal that monohydrocalcite dehydrates directly to calcite as indicated by their similar δ^{18}O and δ^{13}C isotope ratios (Table 1).

Implications of the weddellite transformation

Monohydrocalcite and calcite were identified as the transformation products of weddellite from saguaros throughout southern Arizona. In addition, monohydrocalcite and calcite were found in all decayed cacti in southern Arizona, as well as from cacti as far east as central Texas where yearly rainfall exceeds 75 cm. These widespread occurrences suggest that the Ca oxalate to calcite transformation process is a ubiquitous phenomenon in arid and semiarid environments.

Large quantities of atmospheric C are stored in the Ca oxalate in areas with high saguaro density. For example, there are more than 4000 saguaros at the 40 ha site at Tumamoc Hill near Tucson, Arizona (Pierson and Turner 1998). There is thus an estimated 1.1×10^8 g of weddellite at this site. This weddellite contains 1.6×10^7 g C_{atm}, corresponding to an areal density of 40 g/m^2 C_{atm}. Assuming an average saguaro life span of 140 years, the 1.1×10^8 g of Ca oxalate is equivalent to the release of 1.9 g/m^2/yr of Ca oxalate. In the proposed transformation mechanism, only half of the oxalate C transforms to carbonate in the calcite, equivalent to 2.4 g/m^2/yr of calcite added to the desert environment. The total calcite released will be significantly larger once the contributions from the other cacti are included.

The saguaro-derived calcite will either resolubilize and accumulate in the subsurface Ca-rich soil horizons or break down and be redistributed by wind. The friable nature and small grain sizes of the saguaro-derived calcite suggests that this material can be eroded efficiently and become incorporated in wind-blown dust. Dust is considered one of the main sources of calcite in soils of arid and semiarid regions, with measured accumulation rates of 1 to 5 g/m^2/yr (Péwé et al. 1981; Schlesinger 1982; Naiman et al. 2000 and references therein). This range for calcite accumulation per annum spans the quantity of calcite released to the desert in areas with high saguaro density. Thus, it is likely that a significant proportion of the calcite in dust from southern Arizona is derived from the transformation of the Ca oxalate biominerals from cacti.

Further evidence for a Ca oxalate-derived carbonate component in wind-blown dust is revealed by the δ^{13}C isotopic data, which are in the range of values found for dust in southern Arizona (Naiman et al. 2000). The δ^{13}C data of monohydrocalcite and calcite derived from the weddellite range from -1.65 to 0.76 ‰, which is in the upper range of values for caliche in the South Maricopa Mountain Wilderness (Table 1). The monohydrocalcite and calcite after weddellite also have significantly different δ^{13}C values compared with those of calcite precipitated from ground water in contact with the atmosphere in the Phoenix area (Table 1, pavement calcite).

I identified Ca oxalates in all common species of cacti and in many of the vascular leafy plants of southern Arizona. These oxalates are also a common component of the crustose lichens that are abundant in arid regions (Bungartz pers. com.). Given the widespread nature of Ca oxalates in the environment, there is the potential for these biominerals to contribute significantly to the global C cycling. In contrast to organic matter decomposition in soils, little attention is given to the fate of Ca oxalates released by plants in arid and semi-arid regions. In arid environments, the desert fauna metabolizes the bulk of the atmospheric C bound in the organic matter to CO_2 and water. In contrast, decay of the saguaro, as well as other cacti, adds atmospheric C to the soil as inorganic C via the transformation of the Ca oxalate biominerals. This inorganic C has geologically long soil residence times, thus effectively sequestering the atmospheric C.

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