Santaclaraite, a new calcium-manganese silicate hydrate from California

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Abstract

Santaclaraite, ideally CaMn$_4$Si$_5$O$_{14}$(OH)$_2$·H$_2$O, occurs as pink and tan veins and masses in Franciscan chert in the Diablo Range, Santa Clara and Stanislaus Counties, Calif. It is associated with four unidentified Mn silicates, Mn-howieite, quartz, braunite, calcite, rhodochrosite, kutnohorite, barite, harmotome, chalcopyrite, and native copper. Santaclaraite is triclinic, space group $B1$, $a = 15.633(1)$, $b = 7.603(1)$, $c = 12.003(1)$ Å, $\alpha = 109.71(1)^\circ$, $\beta = 88.61(1)^\circ$, $\gamma = 99.95(1)^\circ$, $V = 1322.0(3)$ Å$^3$, $Z = 4$. The strongest lines of the X-ray powder pattern are $(d, l, hkl)$: $7.044$, $100$, $010$; $3.003$, $84$, $501$; $3.152$, $80$, $410$; $7.69$, $63$, $200$; $3.847$, $57$, $113$, $400$; $3.524$, $39$, $020$. Crystals are lamellar to prismatic (flattened on {100}), with good cleavage on {100} and {010}; H: $6%$; D(calc.) : $3.398$ g/cm$^3$, D(meas.) : $3.31(0.01)$. optically biaxial negative, with $\alpha = 1.681$, $\beta = 1.696$, $\gamma = 1.708$ (all $\pm 0.002$), $2V_\chi = 83$ (±1)$^\circ$. Although chemically a hydrated rhodonite, santaclaraite dehydrates to Mn-bustamite at about 550°C (in air). Santaclaraite is a five-tetrahedral-repeat single-chain silicate and has structural affinities with rhodonite, nambulite, marsturite, babingtonite, and inesite.

Introduction

The new mineral santaclaraite was discovered in 1975 in an abandoned manganese mine in the Diablo Range in northeastern Santa Clara County, Calif., by Messrs. John L. Parnau and Albert L. McGuinness, who brought it to us for investigation. They suspected that the mineral was inesite from its color and prismatic habit, but our studies proved the mineral to be new and to have a crystal structure that helps to clarify the role of hydrogen in pyroxenoids (Ohashi and Finger, 1981). The mineral is named for the County of Santa Clara, the locality of its first occurrence. Specimens of santaclaraite (holotype and cotypes) will be deposited at the Smithsonian Institution (National Museum of Natural History), Washington, D.C. The name and description have been approved by the Commission on New Minerals and Mineral Names, I.M.A. A description given by Ohashi and Erd (1978) of an unnamed new mineral was a preliminary report for santaclaraite.

Occurrence and paragenesis

Although the discoverers of santaclaraite did not disclose the exact location of its occurrence, they have provided us with many specimens from the locality and partial information on the occurrence. The mine is one of about fifty abandoned manganese mines located in Santa Clara, Alameda, San Joaquin, and Stanislaus Counties near their common junction. Nearly all these mines lie within a circle of 16-km radius centered on Mount Boardman at this junction. The mines and the geology of the area were described by Jenkins (1943) and Trask (1950), and a review with later production figures was presented by Davis (1957). The manganese ore bodies in the four-county area are of the Coast Range sedimentary type that occur in chert of the Franciscan Complex (Jurassic to Lower Tertiary).

Our present information from the discoverers is that the abandoned mine in which santaclaraite was discovered is on property that is now private, posted against trespassing, and patrolled by a security system. The mine workings are no longer accessible, and all of the manganese mineral specimens were found on old dumps at this site.

The paragenesis of the specimens that we have seen from this locality is noteworthy in that the more common Mn minerals are scarce or absent and the Mn silicates so far found are all unusual in some respects. It seems worthwhile, therefore, to give a detailed account of the associated Mn minerals. Santaclaraite occurs both as cross-fiber veins (the largest measures 1 cm in width by more than 9 cm in length) and irregular masses (10 cm in
maximum dimension) in Mn-oxide-stained chert and quartz. Though uncommon in its overall occurrence, santaclaraite is the most abundant Mn silicate at this locality. The next most abundant Mn silicate is an unidentified reddish-brown fine-grained mineral that appears to be a member of the friedelite series. Three other unidentified Mn silicates at this locality are similar to, but differ in some respects from, the minerals parsettensite, welinite, and gageite (all currently under study). Mn-howieite is associated with santaclaraite as yellow-brown fibrous veinlets, masses, and small spherules, with \( a = 1.697, \beta = 1.716, \gamma = 1.727 \) (all \( \pm 0.002 \)). Fine-grained rhodochrosite is subordinate to the Mn silicates but is widely disseminated throughout them and the quartz matrix. Calcian kutnohorite and calcian rhodochrosite were found in a single occurrence as small scalenohedra (to 0.6 mm). The central cores of the crystals consist of massive white Ca-kutnohorite \((a = 4.919, c = 16.525\text{Å}; \omega = 1.702, e = 1.518, \text{both} \pm 0.002)\) encrusted with tiny euhedral rhombs of Ca-rhodochrosite \((a = 4.824, c = 16.01\text{Å}; \omega = 1.785 \pm 0.003, e = 1.518 \pm 0.002)\). A strong positive microchemical test was obtained for Mn, but Fe could not be detected. The data indicate about 20 mole percent CaCO\(_3\) in the rhodochrosite, which is near the limit for naturally occurring material (Deer et al., 1962, p. 265-267). All the specimens that we have seen are stained black with a thin coating of X-ray amorphous Mn oxide, although very little of this material is actually present. The Mn mineral that was mined at this locality appears to have been braunite, which occurs as masses and veins, up to 6 cm across in the specimens that we have seen. Other associated minerals are calcite (some manganoan), barite, and rare harmontome, chalcopyrite, and native copper. Some of the quartz is colored dark grayish blue by inclusions of asbestiform riebeckite.

A second occurrence of santaclaraite was discovered at the Buckeye mine (located in sections 2 and 3, T. 5 S., R. 5 E., in Stanislaus County, Calif.). The mineral was identified by Erd in specimens collected in 1942-1944 from the ore body by Dr. Max D. Crittenden, Jr., during his study of the geology of the deposit (Trask, 1950, p. 287-289). Santaclaraite occurs sparsely as pink prismatic crystals up to 3 mm long in quartz veins in tan chert associated with rhodochrosite, the friedelite-like mineral (identical with that of the Santa Clara Co. occurrence), braunite, and very minor chalcopyrite. It is probable that at least some of the "inesite" identified in the mine by Crittenden is actually santaclaraite (Crittenden, oral communication, 1980). The underground workings at the abandoned Buckeye mine are no longer accessible and an attempt to find santaclaraite in the present-day (1981) dumps was unsuccessful.

**Crystallography**

**Morphology**

Santaclaraite occurs principally as radiated lamellar aggregates (Fig. 1) composed of thin prismatic to tabular subhedral crystals, flattened on \( \{100\} \). The rough spherules average about a millimeter in diameter. Where space permits, thick prismatic euhedra, up to a centimeter in length on \( \{001\} \), are developed; several of these are visible in the vug in Figure 1. The mineral also occurs in cross-fiber veins composed of prismatic to nearly fibrous crystals having a length/width ratio up to 40. Forms identified with a two-circle optical goniometer are \( b \{010\}, a \{100\} \) the most prominent form, \( m \{110\}, f \{101\}, g \{301\}, \) and \( h \{401\} \). Simple twinning on \( \{100\} \) is common.

**X-ray data**

The preliminary unit-cell dimensions of santaclaraite were determined from single-crystal X-ray precession photographs using Zr-filtered Mo radiation. Table 1 lists these data, refined by least-squares analysis of the X-ray powder data. The crystal structure of santaclaraite has been determined by Ohashi and Finger (1981); the mineral has centric triclinic symmetry (PI for the primitive cell). An \( I \)-centered cell was employed by Ohashi and Finger for structural comparison of santaclaraite with other pyroxenoids; however, a \( B \)-centered cell is selected here on the basis of morphology for the mineralogic description. Table 1 compares the data for the various settings. The X-ray powder data are shown in Table 2. There is a moderately strong preferred orientation of \( hko \) reflections in the X-ray diffractometer pattern due to the good \( \{010\} \) and \( \{100\} \) cleavages. The intensities observed in powder photographs agree closely with the calculated intensities and so are not listed in Table 2. The effect of the preferred orientation is most noticeable for the lines at \( d = 2.692 \) and 2.939Å, which are the strongest in powder photographs.

Fig. 1. Vuggy radiated pink santaclaraite, with prismatic crystals of tan santaclaraite (larger is 7.5 mm long) projecting into vug at center. Photograph by Lowell Kohnitz, U.S. Geological Survey.
Table 1. Unit-cell data for santaclaraite

<table>
<thead>
<tr>
<th>System</th>
<th>Triclinic</th>
<th>Triclinic</th>
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<tr>
<td>Space group</td>
<td>$\Gamma$</td>
<td>$\Gamma^*$</td>
<td>$\Gamma^*$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>9.738(2)**</td>
<td>10.643(1)</td>
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<td>b (Å)</td>
<td>9.970(1)</td>
<td>10.970(1)</td>
<td>10.784(1)</td>
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<td>c (Å)</td>
<td>7.603(1)</td>
<td>12.003(1)</td>
<td>12.003(4)</td>
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<td>α (°)</td>
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<td>88.6(1)**</td>
<td>110.6(2)**</td>
</tr>
<tr>
<td>β (°)</td>
<td>104.97(1)**</td>
<td>99.95(1)**</td>
<td>89.09(1)**</td>
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<td>γ (°)</td>
<td>161.01(1)</td>
<td>132.01(3)</td>
<td>132.01(4)</td>
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</table>

* Alternative settings used for mineralogical and crystal structural descriptions. Cell transformation matrices are $\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}$ for the $\Gamma$ to $\Gamma^*$ cell and $\begin{bmatrix} 1/2 & 1/2 & 0 \\ 0 & 1/2 & 1/2 \\ 1/2 & 0 & 1/2 \end{bmatrix}$ from the $\Gamma^*$ to $\Gamma$ cell.

** Data obtained from refinement of X-ray powder data (Table 2), using the least-squares program of Appelman and Evans (1973). Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 9.738(2) indicates an esd of 0.002.

† Determined in methylene iodide/acetone mixture checked with a Weissenberg balance.

Table 2. X-ray powder diffraction data for santaclaraite

<table>
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<tr>
<th>hkl</th>
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<td>041</td>
<td>2.993</td>
<td>88.4</td>
<td>3.00</td>
<td>7.00</td>
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</table>

* All lines are indexed to $\theta \leq 2.350^\circ$. Indices from least-squares analysis of X-ray powder data, using the digital-computer program of Appelman and Evans (1973). Intensities calculated by a program of Smith and Holomy (1978).

** X-ray diffractometer conditions are: Chart No. X9177; Cu/NaKα radiatior; NaKα = 1.540598Å; silicon used as internal standard; scanned at 1/4° per minute from 4° to 100° 2θ.

Physical and optical properties

Santacaraite is pale pink (Munsell color 5RP 8/2) or moderate reddish orange (10R 6/6). Although these two color varieties are quite distinctive, we observed no significant differences in their chemical composition or optical properties. The color of the pale-pink variety darkens to orange when exposed to tungsten X-radiation. The mineral is transparent and has a vitreous luster and a very pale pink streak. It is nonfluorescent. Cleavage is good on both {100} and {010}. Its hardness is 6% (Mohs).

Santaclaraite is biaxial negative: $a = 1.681$, $b = 1.696$, $c = 1.708$ (all $\pm 0.002$; Na light); $\alpha = 83(4)$, $\beta = 83(4)$, $\gamma = 83(4)$. The optical orientation is $Z = 21$, $X = -14.5$ in {100} sections. Thick sections of santaclaraite show a weak pleochroism, with $X = $ very pale red, $Y = $ pale red, and $Z = $ pale reddish brown; absorption is $I > Z > X$. The optical properties were determined using a spindle stage with X-ray oriented crystals.

Chemistry

Analyses were made of both pink and tan santaclaraite, using the Geophysical Laboratory MAC electron micro-
probe with an accelerating voltage of 15 kV and a specimen current of 0.05 μA. The results of the analysis of the tan santacalaite are shown in Table 3. As noted above, the analysis of the pink material is so similar that it is not reported here. The matrix corrections made are those proposed by Bence and Albee (1968) and programmed by Finger and Hadidiacos (1972) for the microprobe-analysis system. The standards used (Table 3) were selected on the basis of the beta factor in the Bence-Albee method. There is “superior” agreement (1-Kp/K = +0.002) between the chemical data, optical data, and specific gravity, using the compatibility index of Mandarino (1981) for the Gladstone-Dale relationship.

The formula of santacalaite, obtained by combining the electron-microprobe analysis data of Table 3 with the crystal-structure data of Ohashi and Finger (1981), is:

\[
\text{CaMn}_{4}\left[\text{Si}_{5}\text{O}_{10}\left(\text{OH}\right)\left(\text{OH}\right)_{2}\text{H}_{2}\text{O}\right]
\]

Santacalaite is insoluble or only very slightly soluble in hot concentrated acids. When the mineral is heated in a closed tube, a moderate amount of water is driven off (pH = 5), and the mineral turns light brown; with stronger heating, to about 1000°C, the mineral turns white and nearly opaque.

**Related minerals**

Santacalaite is chemically a hydrated rhodonite, although structurally hydrogen atoms play three different roles (for structural discussion see Ohashi and Finger, 1981). In addition to rhodonite, several minerals are known that are structurally related to santacalaite (Table 4); these minerals all have silicate chains with five tetrahedral repeats and bands of octahedral cations. Inesite, which is visually very similar to santacalaite, is a double-chain silicate (Wan and Ghose, 1978): the others are single-chain silicates.

The number of hydrogen atoms (e.g., per five silicons) of santacalaite is higher than those of babingtonite, nambulite, and marsturite but less than that of inesite. If only chemical formulas are considered, incorporation of hydrogen into an anhydrous formula \(\text{M}^{2+}\text{Si}_{5}\text{O}_{15}\) or \(\text{M}^{2+}\text{Si}_{6}\text{O}_{30}\) can be accomplished by the following changes:

### Table 4. Chain silicate minerals with five tetrahedral repeats

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Idealized chemical formula</th>
<th>Reference to crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Santacalaite</td>
<td>(\text{CaMn}<em>{4}\left[\text{Si}</em>{5}\text{O}<em>{10}\left(\text{OH}\right)\left(\text{OH}\right)</em>{2}\text{H}_{2}\text{O}\right])</td>
<td>[1]</td>
</tr>
<tr>
<td>Rhodonite</td>
<td>(\text{CaMn}<em>{4}\left[\text{Si}</em>{5}\text{O}<em>{10}\left(\text{OH}\right)\left(\text{OH}\right)</em>{2}\text{H}_{2}\text{O}\right])</td>
<td>[2]</td>
</tr>
<tr>
<td>Babingtonite</td>
<td>(\text{Ca}<em>{2}\left(\text{Fe}^{2+},\text{Mn}\right)\text{Fe}^{3+}\left[\text{Si}</em>{5}\text{O}<em>{10}\left(\text{OH}\right)\left(\text{OH}\right)</em>{2}\text{H}_{2}\text{O}\right])</td>
<td>[3]</td>
</tr>
<tr>
<td>Nambulite</td>
<td>(\text{Li}<em>{2}\text{Mn}</em>{4}\left[\text{Si}<em>{5}\text{O}</em>{10}\left(\text{OH}\right)\left(\text{OH}\right)<em>{2}\text{H}</em>{2}\text{O}\right])</td>
<td>[4]</td>
</tr>
<tr>
<td>Marsturite</td>
<td>(\text{NaCaMn}<em>{3}\left[\text{Si}</em>{5}\text{O}<em>{10}\left(\text{OH}\right)\left(\text{OH}\right)</em>{2}\text{H}_{2}\text{O}\right])</td>
<td>[5]</td>
</tr>
<tr>
<td>Inesite</td>
<td>(\text{CaMn}<em>{2}\left[\text{Si}</em>{5}\text{O}<em>{10}\left(\text{OH}\right)\left(\text{OH}\right)</em>{2}\text{H}_{2}\text{O}\right])</td>
<td>[6]</td>
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</table>

### Table 5. Unit-cell data for Ca-bustamite, Mn-bustamite, and dehydrated santacalaite

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Space group</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(V) (Å(^3))</th>
<th>(D) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-bustamite</td>
<td>(\text{Al})</td>
<td>7.846(3)</td>
<td>7.639(5)</td>
<td>3.560</td>
<td>3.086</td>
<td>1.616(2)</td>
</tr>
<tr>
<td>Mn-bustamite</td>
<td>(\text{Al})</td>
<td>7.846(3)</td>
<td>7.639(5)</td>
<td>3.560</td>
<td>3.086</td>
<td>1.616(2)</td>
</tr>
<tr>
<td>Dehydrated santacalaite</td>
<td>(\text{Al})</td>
<td>7.13.0(3)</td>
<td>9.75.3(2)</td>
<td>3.57.2(3)</td>
<td>3.52.1(2)</td>
<td>1.41.0(2)</td>
</tr>
</tbody>
</table>

**Notes:**

- \(\text{Al}\) = Specimens from Broken Hill, W.S.W., Australia, described by Mason (1973). Data obtained from refinement of X-ray powder data (Table 5) using the least-squares program of Appleman and Evans (1973). Error in parentheses is one standard deviation.
- \(\text{Ca}\) = Santacalaite heated in air at approximately 1,000°C for five hours.

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**References:**

<anhydrous phase>  <hydrated phase>
\[
\begin{align*}
\text{M}^3_+ & \quad \text{add H}_2\text{O} \\
\text{M}^3_+ & \quad \text{nambulite} \\
\text{M}^3_+ & \quad \text{namulite and} \\
\text{M}^3_+ & \quad \text{marlurite} \\
\text{M}^3_+ & \quad \text{babingtonite} \\
\text{M}^3_+ & \quad \text{add 5H}_2\text{O} \\
\end{align*}
\]

where \(M\) represents octahedral cations and \([\ )\] unoccupied octahedral site. The reason that there are only nine (instead of ten) octahedra in inesite is related to the location of an inversion center. In inesite the inversion center is at the octahedral site M1 (the sequence is 5-4-3-2-1-2-3-4-5, thus nine in total), whereas in rhodonite it is between two M1 sites (i.e., 5-4-3-2-1-2-3-4-5, thus ten in total).

The structural relations of these pyroxenoid minerals can well understood in terms of different stacking schemes of tetrahedral and octahedral "building blocks", for which three types of hydrogen atoms, as \(\text{H}_2\text{O}\), and \(\text{O}-\text{H}\)
H · · · O, are responsible in the case of santaclaraite (Ohashi and Finger, 1981). The genetic relationships such as hydration and dehydration, however, are not known at present among the minerals listed in Table 4. When santaclaraite is heated, it does not transform to either CaMn$_2$[Si$_2$O$_5$(OH)] or CaMn$_4$[Si$_4$O$_9$], but the tetrahedral repeat length changes, as is discussed in the next section. Thus this relation for santaclaraite is another example of a phase change between pyroxenoids or pyroxenes with different tetrahedral chain repeats (Morimoto et al., 1966, for johannsenite-bustamite; Glasser and Glasser, 1961, for rhodonite-wollastonite; Aikawa, 1979, for rhodonite-pyroxympangite).

**Dehydration to Mn-bustamite**

We found early in our study that santaclaraite dehydrates in air at a low red heat to form Mn-bustamite. This reaction has been described at length by Ohashi and Finger (1981) and, although the mechanism is not discussed further here, it is of interest to compare the dehydration product with naturally occurring bustamite. Unit-cell (Table 5) and X-ray powder diffraction (Table 6) data are listed for dehydrated santaclaraite and for two bustamites from Broken Hill, N.S.W., Australia, that contain 78.8 and 33.8 mole percent CaSiO$_3$ and represent nearly limiting compositions of bustamite (Mason, 1975).

Agreement between the powder diffraction data of dehydrated santaclaraite and these two bustamites is excellent except for the intensity data. The X-ray diffractometer traces of Ca- and Mn-bustamite (Table 6) show a strong preferred orientation due to good cleavages on (100) and (001). The strongest reflection in the calculated pattern (Borg and Smith, 1969) and in X-ray powder photographs prepared from a spherical mount is for d (220). The strongest line, without exception, for diffractometer traces is for d (204). This orientation effect is minimized in the pattern of the Mn-bustamite produced by heating santaclaraite as the transformation is not topotactic (Ohashi and Finger, 1981), and the observed intensities agree much better with those calculated from the crystal structure.

When the mole percentage of CaSiO$_3$ in naturally occurring bustamites is plotted against their molar volumes, the curve is seen to be essentially linear (Fig. 2). The slope of this line differs slightly from, but agrees reasonably well with, that given by Abrecht and Peters (1980, p. 265, Fig. 6). Extrapolation of this line suggests that the Mn-bustamite produced by dehydration of santaclaraite should contain about 24 mole percent CaSiO$_3$ for the molar volume observed. On the other hand, if the bulk composition of dehydrated santaclaraite (17.7 mole percent CaSiO$_3$) represents only Mn-bustamite, then the molar volume should be approximately 35.4 cm$^3$ or have a cell volume of about 7054 A$^3$. That such is not the case suggests that when santaclaraite is dehydrated by heating, it transforms chiefly to Mn-bustamite plus a minor amount of another phase or phases; these minor phases are either X-ray amorphous or insufficiently abundant to contribute to the X-ray diffraction pattern. In any case, the Mn-bustamite produced by heating santaclaraite above 550°C (Ohashi and Finger, 1981) must contain substantially less CaSiO$_3$ than the limiting mole ratio of 1/3 found for naturally occurring bustamite (Mason, 1975; Ohashi and Finger, 1978). Abrecht and Peters (1980), who have synthesized Mn-bustamite containing about 20 mole percent CaSiO$_3$, suggested that this result may indicate disorder in their synthetic high-temperature Mn-bustamite. However, a recent study by Yamanaka and Takéuchi (1981) has shown that a natural rhodonite with 18.10 mole percent CaSiO$_3$ could be transformed into bustamite. The plot of mole percent CaSiO$_3$ versus molar volume for their inverted bustamite plots very near to that of dehydrated santaclaraite in Figure 2.

**Acknowledgments**

We thank Messrs. John L. Parnau and Albert L. McGuinness for the santaclaraite specimens and for furnishing us with a partial description of the discovery site. Permission to visit the Buckeye mine was granted us by Messrs. Rolland Seegers and Manuel Gonzales; specimens from the mine were provided by the late Dr. Max D. Crittenden, Jr. We are indebted to Dr. Brian H. Mason, of the Smithsonian Institution, Washington, D.C., for specimens of Ca- and Mn-bustamite from Broken Hill, N.S.W., Australia. This study was partly supported by National Science Foundation Grant EAR-77-15703. The manuscript bene-
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Manuscript received, June 30, 1982; accepted for publication, May 25, 1983.