Subsolidus phase relations in the system $K_2Ca(CO_3)_2 - Na_2Mg(CO_3)_2$ at 1 kbar:
The fairchildite$\_ss$-buetschliite-eitelite eutectoid

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ABSTRACT
Solid solutions with the fairchildite structure extend from 100 to 42 mol% $K_2Ca(CO_3)_2$ at high temperature, whereas at low temperature there is a very restricted solid solution between buetschliite and eitelite. Fairchildite solid solution is in equilibrium with nearly stoichiometric buetschliite and eitelite at $327 \pm 5 ^\circ C$, $63.5 \pm 1.0$ mol% $K_2Ca(CO_3)_2$, and 1 kbar. The nearly complete immiscibility (<2 mol%) of buetschliite and eitelite and the ability of fairchildite to form wide-ranging solid solutions are discussed in the light of the known crystal structures.

INTRODUCTION
This investigation was undertaken in the course of a comprehensive study of the quaternary system $Na_2Ca(CO_3)_2 - K_2Ca(CO_3)_2 - K_2Mg(CO_3)_2 - Na_2Mg(CO_3)_2$ with the specific objectives of (1) exploring the extent of solid solution between the structurally similar phases buetschliite, $K_2Ca(CO_3)_2$, and eitelite, $Na_2Mg(CO_3)_2$, and (2) determining the extent of solid solution in the high-temperature phase fairchildite. It was already known that fairchildite, $K_2Ca(CO_3)_2$, and nyerereite, $Na_2Ca(CO_3)_2$, are completely miscible at elevated temperatures, giving rise to solid solutions with structural modulation, of which natural nyerereite (McKie and Frankis, 1977) is an example.

The symbols FC, BU, EI will be used to represent the stoichiometric phases fairchildite, $K_2Ca(CO_3)_2$; buetschliite, $K_2Ca(CO_3)_2$; and eitelite, $Na_2Mg(CO_3)_2$. The symbol FC$\_ss$ will be used qualitatively to represent solid solutions between $K_2Ca(CO_3)_2$ and $Na_2Mg(CO_3)_2$ with the fairchildite structure, the subscript ss being replaced by the molar percentage of $K_2Ca(CO_3)_2$ in the solid solution where a quantitative description is appropriate. Likewise a number representing the molar percentage of $K_2Ca(CO_3)_2$ is attached as a subscript to BU or EI to show the composition of a solid solution with the buetschliite or eitelite structure.

EXPERIMENTAL METHOD
The reactants used for synthetic experiments were analytical-grade $K_2CO_3$ and $CaCO_3$, and eitelite crystallized from aqueous solution at 85 $^\circ C$ by the method described by Pabst (1973). The reactants were always finely ground in an agate mortar and dried at 130 $^\circ C$ before being weighed. Each mixture was ground under acetone, dried at 130 $^\circ C$, and stored over $P_2O_5$. An appropriate quantity of the reactant mixture was loaded into a dry Au capsule, which was immediately welded. Cooper et al. (1975) have pointed out that equilibria involving $K_2Ca(CO_3)_2$ are significantly affected by the presence of $H_2O$. The Au capsule was weighed after welding, again after cold pressurization, and finally on completion of the experiment; the few experiments for which the weight was not constant were rejected. All the synthetic experiments were made in Tuttle-type cold-seal pressure vessels.

Reaction in carbonate systems is generally fast even under dry conditions; therefore the duration of these experiments, at least 7 d in all cases, should have been more than adequate to produce equilibrium. Some of the experiments used to determine the eutectoid were made with buetschliite synthesized at 480 $^\circ C$ at 1 atm and eitelite synthesized as indicated above. Certain other low-temperature experiments were preheated for at least 2 d at approximately 650 $^\circ C$ and 1 kbar to yield fairchildite solid solution (with or without quenched liquid) as the starting material for a subsequent experiment of at least 7 d at the chosen temperature and 1 kbar; such experiments are asterisked in Table 1. The experiments used to determine the eutectoid thus involve reversal of phase assemblages.

The product of each synthetic experiment was examined optically and by X-ray powder diffractometry. The products of some experiments were further studied by single-crystal X-ray diffraction methods. The standard diffractometry procedure applied to each experiment was to mix the product with quartz to produce four diffractometer traces in the range of 2$\theta$ from 25$^\circ$-38$^\circ$ using CuK$\alpha$ radiation, the scale being 40 mm per degree of 2$\theta$. The scale was calibrated by measurement of the separation of the 10.1 and 11.0 quartz peaks at 2$\theta$ = 26.664$^\circ$ and 2$\theta$ = 36.576$^\circ$ on traces where neither peak had interference from weak peaks caused by the reaction products. The chosen 2$\theta$ range includes the 0006(m), 10.5(vs), and 11.0(w-m) peaks of buetschliite and eitelite and the 0004(w), 10.3(s), 10.4(m), and 11.0(s) peaks of fairchildite solid solutions.

The composition of buetschliite-eitelite solid solutions

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was determined for measurements of 2θ for the 10.5 and 0006 peaks assuming that d varies linearly with molar composition between the determined values for synthetic 
buetschliite (d,ur: 2.8648 Å, dooor: 3.0257 Å) and syn-
thetic eitelite (d,ur: 2.6036 Å, dooor: 2.7342 Å). Molar composition was always deter-
mined using the strong 10.3 and 11.0 peaks in the range of compositions of the
products of quenching from the two-

Synthesis experiments for FC100 at 559 °C, FC50 at 649.6 °C, FC0 at 651 °C, FC70 at 475 °C, FC90 at 450 °C, and FC50 at 450 °C yielded linear regressions for the values of d for the four

TABLE 1. Selected data necessary to define field boundaries

<table>
<thead>
<tr>
<th>Mix composition</th>
<th>T °C</th>
<th>Product phases</th>
<th>Starting material</th>
</tr>
</thead>
<tbody>
<tr>
<td>K5Ca(CO3)2</td>
<td>BU100 + FC100</td>
<td>K5CO3 + CaCO3, El</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>554.5</td>
<td>BU100 + FC100</td>
<td>K5CO3 + CaCO3, El</td>
</tr>
<tr>
<td>100</td>
<td>549.0</td>
<td>BU100 + FC100</td>
<td>K5CO3 + CaCO3, El</td>
</tr>
<tr>
<td>90</td>
<td>498.6</td>
<td>BU100 + FC100</td>
<td>K5CO3 + CaCO3, El</td>
</tr>
<tr>
<td>90</td>
<td>451.8</td>
<td>BU100 + FC100</td>
<td>K5CO3 + CaCO3, El</td>
</tr>
<tr>
<td>80</td>
<td>399.3</td>
<td>BU100 + FC100</td>
<td>K5CO3 + CaCO3, El</td>
</tr>
<tr>
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<td>361.1</td>
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</tr>
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<td>300.0</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>200.0</td>
<td>BU100 + FC100</td>
<td>K5CO3 + CaCO3, El</td>
</tr>
<tr>
<td>30</td>
<td>100.0</td>
<td>BU100 + FC100</td>
<td>K5CO3 + CaCO3, El</td>
</tr>
<tr>
<td>10</td>
<td>0.0</td>
<td>BU100 + FC100</td>
<td>K5CO3 + CaCO3, El</td>
</tr>
</tbody>
</table>

† Indicates preheating at ~650 °C, 1 kbar.

where X is the molar percentage of K5Ca(CO3)2 in the solid solution. The standard error for compositions determined using the strong 10.3 and 11.0 peaks is better than ±1%. The weaker 0004 and 10.4 peaks were not used for the determination of composition.

Liquids usually quench not to glass but to microcrystalline aggregates in carbonate systems (Cooper et al., 1975). In this system the optical identification of the quench products of liquids is not invariably conclusive, but where it is conclusive the X-ray diffractometer traces exhibit broadening of fairchildite and eitelite peaks and, in some cases, doubling of strong fairchildite peaks. In optically inconclusive cases the broadening of peaks on the diffractometer trace has been taken to be indicative of liquid formation.

RESULTS

Although the system K5Ca(CO3)2-NaMg(CO3)2 is merely a diagonal of the quaternary system NaCa(CO3)2-NaMg(CO3)2-K5Ca(CO3)2-NaMg(CO3)2 rather than a strictly binary system, it is apparent that at temperatures below the solidus it is effectively binary. That the extent of solid solution in the buetschliite and eitelite phases is restricted to <2% allows these phases to be treated as binary to an acceptable level of approximation. The linearity of the variation of the values of d, and consequently of unit-cell dimensions, with molar composition in the single-phase field of the fairchildite solid solution, coupled with the observation by diffractometry and optical inspection that the field is truly single phase, extends the temperature range of effective binary behavior up to the solidus. The solidus is limited at one extremity by the melting point of fairchildite, determined by Cooper et al. (1975) as 809 °C at 1 kbar. The melting point of eitelite, which limits the solidus at its other extremity, has been determined by Eitel and Skaliks (1929) as 677 °C at 1.22 kbar; if dT/dP is taken to be of approximately the same magnitude as that determined by Koster van Groos and Wyllie (1966) for the melting point of Na5CO3, 16 °C per kbar, then the melting point of eitelite at 1 kbar is reduced by about 4 °C to 673 °C. The temperature of the transformation of fairchildite to buetschliite in K5Ca(CO3)2 at 1 kbar has been determined by Cooper et al. (1975) as 547 °C and in this work as 552 ± 3 °C.

Melting relations appear to be quaternary in that the compositions of the products of quenching from the two-phase field of fairchildite solid solution and liquid, determined by use of the regression equations of values of d for the binary fairchildite solid solutions given above, are inconsistent with the known bulk composition. The fairchildite solid-solution liquidus is therefore shown as a broken line in Figure 1. The eitelite liquidus and the isothermal solidus through the eutectic are likewise shown as broken lines because their determination was not an objective of this study. The eutectic temperature lies within the broad limits of 557 °C and 501 °C.

The data necessary to define the subsolidus field boundaries, selected from 51 consistent experiments, are...
given in Table 1, and the resultant phase diagram is shown in Figure 1. Subsolidus field boundaries have been determined to better than ±1 mol% and ±1 °C.

Three aspects of this system are of interest. One is that the fairchildite solid solution is shown by single-crystal X-ray precession photographic study to be strictly hexagonal across the compositional range from 100 to 42 mol% K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>, in contrast to the K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>-Na<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub> system, where modulated structures of orthorhombic symmetry occur over most of the compositional range (McKie and Frankis, 1977). The second point of interest is the occurrence of a eutectoid, common in alloy systems but otherwise unusual. At the eutectoid, the fairchildite solid solution of composition 63.5 mol% K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub> is in equilibrium with buetschliite solid solution [98 mol% K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>] at 327 ± 5 °C. The third point of interest is the severely restricted extent of solid solubility between the low-temperature phases buetschliite and eitelite in contrast to the wide-ranging compositional extent of fairchildite solid solutions in this system and in the system K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>-Na<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>.

The structures of buetschliite and eitelite differ, apart from dimensions, only in the rotation of carbonate groups so that the mirror planes observed in buetschliite do not exist in eitelite (Knobloch et al., 1980). The CaO<sub>6</sub> coordination polyhedron, a distorted octahedron, in buetschliite is merely rotated through 14.45° about [0001] to become the MgO<sub>6</sub> coordination polyhedron in eitelite (Fig. 2). The significance of the carbonate rotation becomes apparent when the coordination of the alkali cations is considered. In buetschliite the K<sub>2</sub>O polyhedron has six equidistant O atoms (of three carbonate groups) on one side and three at a slightly greater distance on the other (Fig. 3). The carbonate rotation in eitelite causes the six alkali-O distances to be alternately lengthened and shortened, so that the coordination polyhedron NaO<sub>6</sub> has the form of a distorted octahedron, strictly a trigonal antiprism. It is apparent from Figure 3 that without rotation of the carbonate groups a Na-O distance as short as 2.337 Å, as found in eitelite (Knobloch et al., 1980), would be incompatible with the separation of carbonate groups, which is determined by the size of the MgO<sub>6</sub> octahedron. The conclusion that the nature of the univalent rather than that of the divalent cation determines whether the buetschliite or the eitelite structure is formed is supported by the observation that K<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> has the buetschliite structure (Hesse and Simons, 1982).

That the fairchildite structure can tolerate substitution of Na<sup>+</sup> for K<sup>+</sup> and of Mg<sup>2+</sup> for Ca<sup>2+</sup> would appear to be
Fig. 4. The CaCO$_3$ sheet at $z = 0$ in fairchildite is shown in plan on (0001). Ca$^{2+}$ is represented by solid circles. The unit cell is outlined by dotted lines. The section of the Ca coordination polyhedron and the carbonate groups are shaded.

due to the presence of (0001) sheets of cations and carbonate anions (Fig. 4), each cation being linked to six O atoms (of three carbonate groups) with the same $z$ coordinate in the hexagonal unit cell (Pertlik, 1981). The same structural motif occurs in high nyerereite, where the cations can be identified as Ca$^{2+}$ (McKie and Frankis, 1977), and in $\alpha$-Na$_2$CO$_3$ (Dubbeldam and de Wolff, 1969) and $\alpha$-K$_2$CO$_3$ (Becht and Struikmans, 1976). In the alkali carbonates these MCO$_3$ sheets are linked by alkali cations, whereas in fairchildite the linkage is through a sandwich of cations (dominantly or wholly K$^+$) and disordered anions.

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**REFERENCES CITED**


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