

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

DUNCAN MCKIE

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, England

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 ± 5 °C, 63.5 ± 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 °C by the method described by Pabst (1973). The reactants were always finely ground in an agate mortar and dried at 130 °C before being weighed. Each mixture was ground under acetone, dried at 130 °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 sig-

nificantly 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 °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 °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 2θ from 25°–38° using $CuK\alpha$ radiation, the scale being 40 mm per degree of 2θ . 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 2θ 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

TABLE 1. Selected data necessary to define field boundaries

Mix composition mol% $K_2Ca(CO_3)_2$	T °C	Product phases	Starting material
100	554.5	BU ₁₀₀ + FC ₁₀₀	K_2CO_3 + CaCO ₃
100	549.0	BU ₁₀₀	K_2CO_3 + CaCO ₃
90	498.6	BU ₉₉ + FC ₈₈	K_2CO_3 , CaCO ₃ , El
90	451.8	BU ₉₉ + FC ₇₇	K_2CO_3 , CaCO ₃ , El
90	399.3	BU ₉₈ + FC ₇₀	K_2CO_3 , CaCO ₃ , El
80	651.1	FC ₉₀	K_2CO_3 , CaCO ₃ , El
80*	350.2	BU ₉₉ + FC ₆₅	FC ₈₀
70	650.1	FC ₈₈ + L	K_2CO_3 , CaCO ₃ , El
70	335.2	BU ₉₈ + FC ₆₄	BU, El
60*	300.0	BU ₉₈ + El ₀	FC ₈₈ + L
50	450.1	FC ₅₀	K_2CO_3 , CaCO ₃ , El
50	401.9	FC ₆₅ + El ₁	K_2CO_3 , CaCO ₃ , El
50	360.8	FC ₆₉ + El ₂	BU, El
50	320.7	BU ₉₈ + El ₁	BU, El
40	557.7	FC ₈₈ + L	K_2CO_3 , CaCO ₃ , El
20	600.3	L	K_2CO_3 , CaCO ₃ , El
10*	340.6	FC ₈₂ + El ₁	L

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

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 ($d_{10.5} = 2.8648 \text{ \AA}$, $d_{0006} = 3.0257 \text{ \AA}$) and synthetic eitelite ($d_{10.5} = 2.6036 \text{ \AA}$, $d_{0006} = 2.7342 \text{ \AA}$). The molar percentage of $K_2Ca(CO_3)_2$ in the solid solution is then given by $(d_{10.5} - 2.6036)/0.002612$ and by $(d_{0006} - 2.7342)/0.002915$. Molar composition was always determined from both peaks and found to be consistent within $\pm 0.5\%$.

Since the fairchildite solid solution does not extend right across the compositional range to $Na_2Mg(CO_3)_2$, compositions made up at intervals of 10 mol% between FC₁₀₀ and FC₅₀ were held at temperatures within the stability field of the solid solution. For each composition the 11.0, 10.3, 10.4, and 0004 peaks were measured. At the composition FC₁₀₀, the 0004 peak interferes with the 10.1 peak of the quartz standard; but the 2θ values for all four fairchildite peaks were determined by measuring the difference in 2θ between the 10.3 and 0004 peaks of fairchildite on a set of diffractometer traces made without addition of the quartz standard and then taking into account the relative intensities of the quartz 10.1 and fairchildite 0004 constituents of the combined peak. Interference with the standard peaks does not occur at other compositions.

Synthesis experiments for FC₁₀₀ at 559 °C, FC₉₀ at 649.6 °C, FC₈₀ at 651 °C, FC₇₀ at 475 °C, FC₆₀ at 450 °C, and FC₅₀ at 450 °C yielded linear regressions for the values of d of the four fairchildite solid-solution peaks in the range of 2θ from 25° to 38° for $CuK\alpha$ radiation:

$$d_{0004} = 3.0765 + 0.002476X$$

$$d_{10.3} = 2.9449 + 0.002373X$$

$$d_{10.4} = 2.4911 + 0.001970X$$

$$d_{11.0} = 2.4397 + 0.002019X$$

where X is the molar percentage of $K_2Ca(CO_3)_2$ in the solid solution. The standard error for compositions determined using the strong 10.3 and 11.0 peaks is better than $\pm 1\%$. 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 $K_2Ca(CO_3)_2$ - $Na_2Mg(CO_3)_2$ is merely a diagonal of the quaternary system $Na_2Ca(CO_3)_2$ - $K_2Ca(CO_3)_2$ - $K_2Mg(CO_3)_2$ - $Na_2Mg(CO_3)_2$ 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 Skalik (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 Na_2CO_3 , 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 $K_2Ca(CO_3)_2$ 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

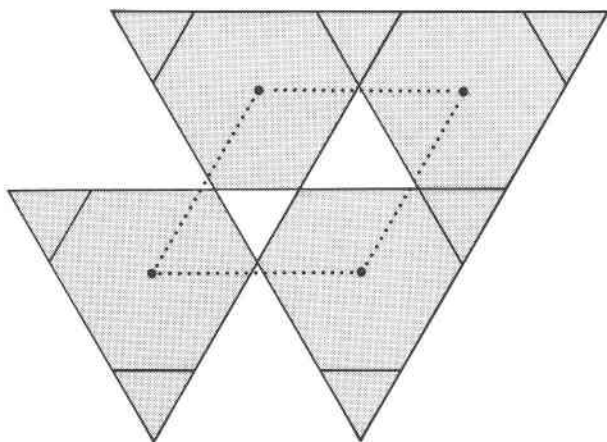


Fig. 4. The $CaCO_3$ sheet at $z = 0$ in fairchildite is shown in plan on (0001). Ca^{2+} is represented by solid circles. The unit cell is outlined by dotted lines. The section of the Ca coordination polyhedron and the carbonate groups are shaded.

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 α - Na_2CO_3 (Dubbeldam and de Wolff, 1969) and α - K_2CO_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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