

## Thermodynamics of mixing of liquids in the system $\text{Ca}_3(\text{PO}_4)_2\text{--CaCl}_2\text{--CaF}_2\text{--Ca}(\text{OH})_2$

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**Abstract**—Molten calcium halide and hydroxide salts may be used as flux and reactants in determining apatite exchange equilibria and solid solution behavior. New experimental data and published phase equilibria are used to determine a thermodynamic model of melts and solids along the binary joins of the anhydrous apatite system  $\text{Ca}_3(\text{PO}_4)_2\text{--CaCl}_2\text{--CaF}_2\text{--Ca}(\text{OH})_2$ . In this model, melt components are expressed as  $\text{Ca}_{0.5}X$ , where  $X$  is hydroxide or a halogen, or as  $\text{Ca}_{1.5}\text{PO}_4$ . The derived binary interaction parameters ( $W_G$ 's) are sufficient to describe deviations from Raoultian behavior for the data. Standard state data are derived for molten  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}_3(\text{PO}_4)_2$ , and for the intermediate compounds  $\text{CaClF}$ ,  $\text{CaClOH}$ , and  $\text{Ca}_2\text{PO}_4\text{Cl}$ .

Melts in the  $\text{CaCl}_2\text{--CaF}_2$  system show ideal mixing behavior, while the calcium hydroxide-bearing molten salts form asymmetric regular solutions. The hydroxide-bearing melts show the small positive enthalpies of mixing typical for mixed-anion salts. Similar behavior is measured in simpler molten salt mixtures. The positive deviations from Raoultian behavior are not a mathematical artifact of the model.

Data are less extensive for the salt-phosphate systems but cover the essential portions of the systems where salt to phosphate ratios are high. The mixtures of the molten salts and phosphate salts show large negative enthalpy interaction parameters ( $W_H$ ), as is expected in eutectic systems which mix a high-melting-point crystal with a low-melting-point flux. Adequate reproduction of the data requires that some entropy interaction parameters be negative, although small. This implies the presence of ordering in the melt, which is manifested in more polymerized phosphate liquids and glasses as halogenated and hydroxylated orthophosphate and pyrophosphate species.

Results of the model indicate that the quaternary system is a good choice for determination of activity-composition relations for the apatites. Comparison of common sources of standard state thermodynamic data (ROBIE et al., 1979; JANAF, CHASE et al., 1985; CODATA, GARVIN et al., 1987) shows that the data for the salts are very similar where they are not identical. At temperatures below 900°C in the ternary systems, liquid compositions will be on or near the apatite-crystalline salt cotectics, and dissolve less than 1 mol%  $\text{Ca}_3(\text{PO}_4)_2$ . This makes  $\text{CaCl}_2\text{--CaF}_2$  mixtures excellent candidates for determination of unambiguous apatite activity-compositional relations. Only the  $\text{Ca}(\text{OH})_2$  liquidus is strongly affected by the addition of phosphate, but this effect is closely described by a regular solution model.

### INTRODUCTION

THE MINERAL APATITE ( $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{OH}, \text{Cl})$ ) (fluorapatite, FAp; hydroxylapatite, HAp; and chlorapatite, ClAp) offers a means to monitor fluid behavior in many geochemical regimes. However, the activities of endmember components in solid solutions remain largely unmeasured. In an earlier paper (TACKER and STORMER, 1989), we examined data available in the literature and determined standard state data for chlorapatite from a subset of the data of KORZHINSKIY (1981). These data are not without shortcomings. The temperature range is restricted to 500–700°C; so use in magmatic environments requires extrapolation. The entire range of solid solution was not synthesized at all conditions for these ClAp-HAp experiments, and the FAp-HAp experiments are even more limited in composition as well as being poorly reversed.

Determination of these relationships presents an interesting problem in experiment design. FAp-ClAp experiments must be performed under anhydrous conditions to avoid introduction of HAp. The experiments should also be performed under conditions where nonstoichiometry of the products is

limited or nonexistent, for stoichiometry problems have long plagued the experimental studies of apatites (YOUNG, 1980; TACKER and STORMER, 1989).

The most common experimental tactic, use of Ag-AgCl (or Ag-AgF) buffers in conjunction with external hydrogen buffers, introduces its own particular problems. High and low hydrogen fugacities may be difficult to maintain (CHOU, 1986; CYGAN and CHOU, 1991). Some buffers have very small buffer capacities (e.g., magnetite-hematite; CHOU, 1987). All of these buffers are limited in applicability to the temperatures where diffusion of hydrogen through capsule material is possible. Even though KORZHINSKIY (1981) used very low hydrogen fugacity buffers, the entire range of solid solution was not synthesized. A further difficulty lies in possible interaction between the Ag-AgCl buffer and the phosphates, as phosphates and phosphate glasses have a large affinity for Ag (WONG and ANGELL, 1976). Simultaneous buffering of HCl and HF is very cumbersome. These experiments may not be carried out in anhydrous environments due to their very nature.

Another problem presented is that apatite is inherently resistant to reequilibration under hydrothermal conditions. LATIL and MAURY (1977) showed clearly that FAp was quite resistant to re-equilibration in Cl-bearing aqueous fluids. Hydroxyapatite would partially re-equilibrate with a fluorine-

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bearing aqueous fluid, but not with one containing chlorine. FARVER and GILLETTI (1989) report that FAp does not react to form HAp in aqueous experiments at temperatures up to 1200°C. TACKER and STORMER (1989) noted that in the experiments of KORZHINSKIY (1981), FAp endmembers barely reacted at all in "reversal" experiments on the FAp-HAp join. The resistance to re-equilibration under hydrothermal conditions is a reflection of the low solubility of the apatites in aqueous fluids. At pressures below 6 kbar, the apatites exhibit retrograde solubility (VALYASHKO et al., 1968; MENGEOT et al., 1973; ROUFOSSE et al., 1973; RUSZALA and KOSTINER, 1975). In plainer terms, they are less soluble at high temperatures than at low. Achieving equilibrium compositions from endmember starting materials will require that diffusion or recrystallization occur.

The halogen compositions of the apatites are relatively immune to diffusive reequilibration because the *c*-axis channel that contains the anions does not allow enough room for the atoms to make coordinated jumps past one another (ROYCE, 1974). Diffusion along *a* is possible but much slower. Rapid diffusion is possible if a unidirectional flux of the halogens along *c* is accompanied by an opposing motion of vacancies, although the anions will not change relative positions (ROYCE, 1974). This occurs in the electrical field imposed on the apatite during electron microbeam analysis (STORMER et al., 1991, 1993). It may also be possible within the field generated by DC furnace elements during high temperature experiments, in which case diffusion may be attributable to furnace configuration rather than temperature.

Reaching equilibrium in the apatites will therefore require recrystallization. The use of molten salts as both fluxes and reactants offers a solution to the problems of buffering and recrystallization. At high salt to mineral ratios, the composition of the salt is essentially unchanged, although the mineral composition may shift significantly. The molten salt solution may approximate a "buffer" as changes in the salt composition approach zero and thermodynamic invariance. A similar technique was used by FERRY and SPEAR (1978) for examining garnet-biotite equilibria at high ratios of garnet to biotite. The molten salts are thermodynamically simple (KLEPPA, 1977, 1987) and easily studied by standard quenching experiments. Most important, it is only in molten salts that stoichiometric monoclinic chlorapatites (ClAp) have been synthesized (PRENER, 1967, 1971). Preliminary experiments with molten salts yield euhedral apatites up to 0.1 mm by 0.04 mm, indicating substantial recrystallization of the starting materials.

We chose the system  $\text{Ca}_3(\text{PO}_4)_2\text{-CaCl}_2\text{-CaF}_2\text{-Ca}(\text{OH})_2$  in which to study the mineral apatite for the reasons given above. One of our goals is to determine the activity-compositional relationships of the F-, Cl-, OH-bearing apatites at magmatic temperatures. Another is to extend and refine standard state data for the chlorapatite endmember. Meeting these goals requires a thermodynamic model of the solids and the liquids in the system, with special attention paid to possible nonideal mixing in these solutions.

Earlier studies in the system  $\text{Ca}_3(\text{PO}_4)_2\text{-CaCl}_2\text{-CaF}_2\text{-Ca}(\text{OH})_2$  have been conducted by PLATO (1906) and NACKEN (1912). Much data already exists on the binary subsystems that bound this quaternary (BIGGAR, 1966, 1967;

WENTZ et al., 1969; REUTOVA and LUKASHENKO, 1971; BERAK and TOMCZAK-HUDYMA, 1972; EPPERLEIN and LEHMANN, 1973, 1975). There were no data on the join  $\text{Ca}(\text{OH})_2\text{-CaCl}_2$ . The  $\text{Ca}(\text{OH})_2$  liquidus for the join  $\text{Ca}(\text{OH})_2\text{-CaF}_2$  (Fig. 1a; GITTINS and TUTTLE, 1964; also used by BIGGAR, 1967) was not in agreement with other determinations of the melting point of  $\text{Ca}(\text{OH})_2$  (WYLLIE and TUTTLE, 1959, 1960), although both studies agree well on the fluorite liquidus and the eutectic position. Here we present new data on the  $\text{Ca}(\text{OH})_2$  liquidus of the  $\text{CaF}_2\text{-Ca}(\text{OH})_2$  join and on the subsystem  $\text{CaCl}_2\text{-Ca}(\text{OH})_2$  (Fig. 1b). The data are then integrated into an internally consistent thermodynamic model.

## METHODS

### Experimental

Most experiments were conducted at NASA Johnson Space Center. Containers were 2.5 mm outer diameter Pt capsules, sealed by arc-welding. Stellite 25 cold-seal pressure vessels were used throughout. Pressures were measured via an in-line Heise gauge and set at 1 kbar with Ar. Temperatures were measured continuously by internal chromel-alumel thermocouples, calibrated against the melting point of Au. Chlorine analysis was performed as end-point titration on a digital chloridometer. A few experiments were also performed at the California Institute of Technology to check the results of earlier experiments, but used identical methods.

Sample preparation and handling were difficult due to the deliquescent nature of the materials. All powders were stored in a vacuum oven above 100°C. Weighing, mixing, and loading of the powders was conducted in a glove bag under dry nitrogen atmosphere. In each weighing session, a "warning" sample was prepared by sprinkling  $\text{CaCl}_2$  powder on a paper towel inside the glove bag. A large wet spot formed immediately on the paper towel if any water was present in the atmosphere. If this occurred or if the powders were observed to be gaining weight on the scales, the session was immediately aborted and the powders redried overnight. Atmospheric water could be eliminated by repeatedly purging the glove bag, introducing the sample containers into the bag at temperatures above 100°C, purging the bag yet again and maintaining it at a pressure slightly greater than atmospheric. Capsules were loaded, crimped, and clipped inside the glove bag, providing a mechanical seal prior to arc-welding. Capsules that opened during welding were discarded, as were capsules that gained weight during a boiling test, or lost weight during the experiment. No moisture was observed in run products, and no evidence of a free aqueous "vapor" phase (meniscus or bubbles) was found.

Run products were examined as grain mounts under index oils on a standard petrographic microscope. X-ray diffraction was used to identify unknown crystalline phases. Stable crystalline phases were euhedral, and quench phases clearly identifiable by their skeletal or dendritic habit. Portlandite ( $\text{Ca}(\text{OH})_2$ ) was recognizable by its trigonal crystal habit and uniaxial negative interference figure. No isotropic CaO was observed, except in capsules that failed at temperature. Hydrophyllite ( $\text{CaCl}_2$ ) formed large, optically continuous crystals that occasionally stretched the length of the capsule, quite distinct from the small needles precipitated during quench. An intermediate compound was identified as  $\text{CaClOH}$  through XRD and optical methods (OSWALD and FEITKNECHT, 1961; MARKOVA, 1973; WESTMAN et al., 1981). Crystals of  $\text{CaClOH}$  tended to be elongated parallel to the *c*-axis, with striations also parallel to *c*. These crystals were optically positive.

### Thermodynamic Methods

#### Choice of standard state data

The standard state for all components is that of the pure substance at 298.15 K and 1 bar, except for molten  $\text{Ca}(\text{OH})_2$ , for which it is 298.15 K and 1000 bars. Standard state data for the crystalline solids

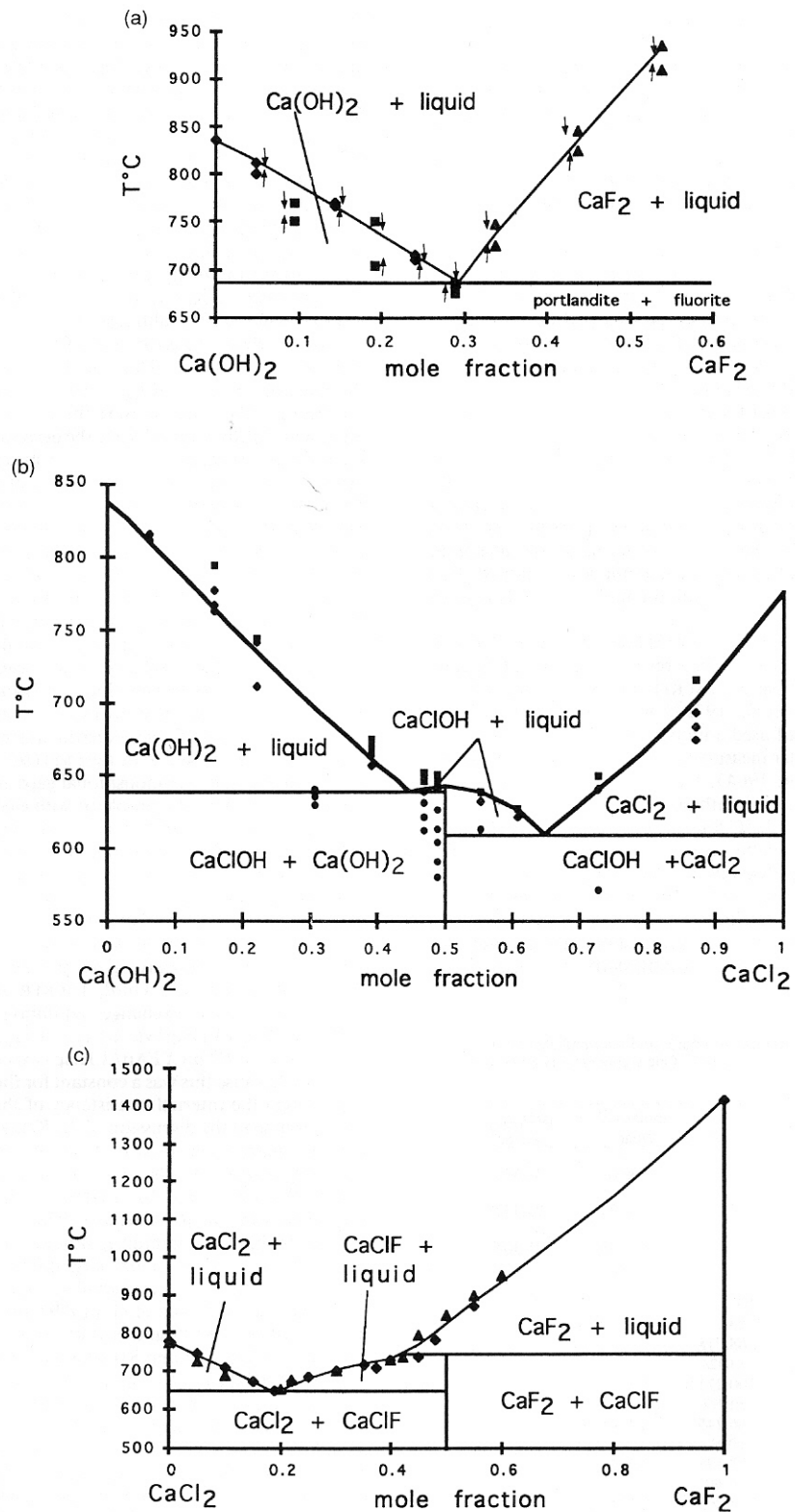


FIG. 1. Experimental data for the molten calcium salts. In all diagrams, the solid line is the calculated liquidus. (a) the system  $\text{Ca(OH)}_2$ - $\text{CaF}_2$ . Diamonds are the data from this study. Squares are the data of GITTINS and TUTTLE (1964), triangles of BIGGAR (1967). Arrows show the direction of the reversal. (b) The join  $\text{CaCl}_2$ - $\text{Ca(OH)}_2$ . Dots are melt absent, diamonds crystal and melt, squares melt only. Portlandite systems are at one kilobar pressure. (c) The join  $\text{CaCl}_2$ - $\text{CaF}_2$  at 1 bar pressure. Triangles are data of REUTOVA and LUKASHENKO (1971), diamonds are data of WENTZ et al. (1969). Errors in the temperatures are generally  $\pm 5^\circ\text{C}$ .

of interest are taken from ROBIE et al. (1979), and heat capacities for the molten salts from JANAF (CHASE et al., 1985) (Table 1). The molten salts tabulated in JANAF show constant heat capacities, but the Gibbs free energies of the liquids are calculated from the melting point to the standard state using the crystalline heat capacity function. The standard state data for liquid  $\text{CaCl}_2$  and  $\text{CaF}_2$  were recalculated from the JANAF data by projecting the enthalpy and entropy to the standard state at the measured constant heat capacity. These recalculated standard state data were used for the purposes of comparison.

The heat capacity functions used herein were not extrapolated beyond the limits of their measurement, except in the case of crystalline  $\text{Ca}(\text{OH})_2$ . Comparison of the heat capacity function of crystalline  $\text{Ca}(\text{OH})_2$  with other sources of data showed no unexpected excursions. Therefore, we did not recalculate the data to the forms used by BERMAN and BROWN (1985), which would allow more reliable extrapolation should it be required.

Molar volumes for the apatites are based on the unit cell data of SUDARSANAN and YOUNG (1978). Other unit cell measurements used were GOLDBLATT et al. (1967) for  $\text{Ca}_2\text{PO}_4\text{Cl}$ , WESTMAN et al. (1981) for  $\text{CaClOH}$ , and LIEBICH and NICOLLIN (1977) for  $\text{CaClF}$ . Molar volumes of liquid components  $\text{CaCl}_2$  and  $\text{CaF}_2$  were calculated from the dependence of the fusion temperature on pressure (JACKSON, 1977). The melting of  $\text{Ca}(\text{OH})_2$  does not occur at low pressures; hence, the molar volume of the liquid could not be determined. This resulted in the choice of standard state for molten  $\text{Ca}(\text{OH})_2$  given above.

Thermodynamic data for the apatites is that adopted by TACKER and STORMER (1989). In the original review of the standard state data sources for hydroxylapatite (TACKER and STORMER, 1989), it was concluded that ROBIE et al. (1979) has selected a source (EGAN et al., 1950, 1951) that had used a monoclinic hydroxylapatite. Enthalpy of formation was later measured on these same samples (ROBIE et al., 1979, cite KRAMER, 1964). Later research (YOUNG, 1980) has shown that the method of synthesis used by EGAN et al. (1950, 1951), i.e., precipitation at  $25^\circ\text{C}$  followed by treatment at  $950^\circ\text{C}$  in water-rich atmosphere, reliably converts hexagonal HAP to its monoclinic form by filling all available sites with hydroxides. Therefore, the data of EGAN et al. (1950, 1951) should be used as the benchmark HAP standard state data.

TACKER and STORMER (1989) derived standard state data for chlorapatite from the experiments of KORZHINSKIY (1981), excluding

data from the 4 kbar experiments and the  $\text{CuO-Cu}_2\text{O}$  buffered experiments. Thermodynamic analysis of the data shows that the results are somewhat scattered (see Fig. 3 of TACKER and STORMER, 1989). The aims of the current study are to test for nonideal mixing in apatite solid solutions and to derive better standard state data for ClAp. We use the original results from TACKER and STORMER (1989) to examine the extent of nonideal mixing in the system whitlockite-hydroxylapatite-portlandite-fluorite with the intention of further refining the data when experiments in the ternary systems are finished. Although the temperatures are somewhat out of the original calibration range they compare well with the other apatite data (see below).

The apatite thermodynamic data of TACKER and STORMER (1989) data has been criticized as "not internally consistent" (ZHU and SVERZHINSKY, 1991), although their assertion was not substantiated and is completely in error. TACKER and STORMER (1989) derived standard state data for ClAp from the data of ROBIE et al. (1979) by the reaction  $\text{HAp} + \text{HCl}_{(g)} = \text{ClAp} + \text{H}_2\text{O}_{(g)}$ . The three known quantities in the equation were the values of ROBIE et al. (1979); it is mathematically impossible for the derived ClAp data to be internally inconsistent. Fugacity data for water measured by BURNHAM et al. (1969) were used in the calculations of equilibrium constants in TACKER and STORMER (1989). This does not introduce inconsistency as BURNHAM et al. (1969) derived absolute fugacities from measured volumes, not from any one standard state. This point is discussed thoroughly in WOOD and FRASER (1978).

Any discussion of "internal consistency" of our examination of the HAP-FAP experiments is very nearly irrelevant, for three reasons. First, in the examination of experimental results of KORZHINSKIY (1981) for HAP-FAP exchange, it was readily apparent that equilibrium was not approached (see Fig. 5 of TACKER and STORMER, 1989). Analytical error is given as  $\pm 4$  mol% (KORZHINSKIY, 1981). At the  $1\sigma$  level, only one of the six experimental pairs in the 500 and  $600^\circ\text{C}$  experiments can be said to be reversed (see Table 2 of KORZHINSKIY, 1981). In the others, compositional gaps are present up to 21 mol%. Second, there are severe problems with electron microprobe analysis of F in apatite (STORMER et al., 1991, 1993). Hydroxylapatite calculated by the difference method is of uncertain value, if not useless. The compositional gaps did not deter ZHU and SVERZHINSKY (1991) from using these experiments to calculate standard state data for HAP and comparing it to that derived from the experiment of BIGGAR (1967). The agreement of data derived from these two sets of experiments is not impressive given the fact that the latter were compositionally unreversed. Third, TACKER and STORMER (1989) displayed the F-OH exchange equilibria on a plot of  $\Delta G_{T,P} + RT\ln(X_{\text{FAP}}/X_{\text{HAP}})$  vs.  $X_{\text{HAP}}^2 - X_{\text{FAP}}^2$ . The spread of data points on the  $\Delta G_{T,P} + RT\ln(X_{\text{FAP}}/X_{\text{HAP}})$  axis is unaffected by the choice of  $\Delta G_{T,P}$ , because this was a constant for the isothermal experiments.

Although the internal consistency of the thermodynamic data is not germane to the discussion of the KORZHINSKIY (1981) data, the thermodynamic data used in TACKER and STORMER (1989) were internally consistent. The enthalpy of formation for FAP used was that of WESTRICH and NAVROTSKY (1981), which was originally calculated using the ROBIE et al. (1978) thermodynamic tabulations (H. Westrich, pers. commun.), although it was not cited correctly in the bibliography. Even though large differences should not have been introduced in the subsequent tabulations, these data were recalculated using the data of ROBIE et al. (1979) and the identical calculation methods of WESTRICH and NAVROTSKY (1981). The updated data were used in TACKER and STORMER (1989), and also are used here.

The ClAp data TACKER and STORMER (1989) were used for philosophical reasons as well. The KORZHINSKIY (1981) experiments represent the best available data base for ClAp, and arguments for complete rejection of the experiments (ZHU and SVERZHINSKY, 1991) are unconvincing. There is no evidence for total disequilibrium in the buffers used. Although hydrogen exchange equilibrium may not have been present, it is likely that steady state conditions were achieved. We feel the use of these data is preferable to extrapolating single data points and assumed entropies based on structurally dissimilar minerals.

Questions regarding the internal consistency of data and model-dependence of results lead to the comparison of data from ROBIE et al. (1979), JANAF (CHASE et al., 1985), and CODATA (GARVIN et al., 1987). Heat capacities ( $C_p$ ), enthalpies and entropies of the elements, crystalline solids, and liquids in the buffer system  $\text{CaCl}_2$ -

**Table 1.** Standard state data derived for liquids and intermediate compounds using model parameters given in Table 4. One sigma error is given beneath each value.

	$\Delta H^0$ kJ/mol	$S^0$ J/molK	molar vol. J/bar	$\Delta H_{\text{fusion}}$ kJ/mol
<b>Solids</b>				
$\text{CaClOH}$	-799.589 $\pm 0.004$	130.348 $\pm 0.158$	3.8562	34.644
$\text{CaClF}$	-1020.465 $\pm 0.293$	83.14 $\pm 2.76$	3.113	29.402
$\text{Ca}_2\text{PO}_4\text{Cl}$	-233.416 $\pm 1.284$	420.836 $\pm 6.016$	7.0333	26.303
<b>Liquids</b>				
$\text{CaCl}_2^\dagger$	-756.183 $\pm 1.3$	101.557 $\pm 4.0$	5.124	
$\text{CaCl}_2^\ddagger$	-770.152 $\pm 0.218$	88.018 $\pm 1.128$	5.124	
$\text{CaCl}_2^*$	-757.308 $\pm 0.218$	100.271 $\pm 1.128$	5.124	
$\text{CaF}_2^\dagger$	-1170.937 $\pm 6.3$	66.245 $\pm 0.33$	2.734	
$\text{CaF}_2^\ddagger$	-1196.547 $\pm 0.482$	52.195 $\pm 0.381$	2.734	
$\text{CaF}_2^*$	-1178.292 $\pm 0.482$	63.065 $\pm 0.381$	2.734	
$\text{Ca}(\text{OH})_2^*$	-995.737 $\pm 0.190$	28.470 $\pm 0.839$		25.416
$\text{Ca}_3(\text{PO}_4)_2$	-3431.223 $\pm 0.0$	862.92 $\pm 0.0$		39.999

Notes:

$^\dagger$  Data from JANAF (CHASE et al., 1985).

$^\ddagger$  Data determined with a  $\text{CaX}_2$  ( $X=\text{Cl}, \text{F}, \text{OH}$ ) molten salt model.

\* Data determined with a  $\text{Ca}_{0.5}\text{X}$  ( $X=\text{Cl}, \text{F}, \text{OH}$ ) molten salt model.

CaF<sub>2</sub>-Ca(OH)<sub>2</sub> are identical in most cases. In the cases where the data are not identical, they are so similar as to be indistinguishable on our graphics software, unless plotted as differences on an expanded-scale chart. These differences are less than 1  $\sigma$  reported errors, and far less than 2  $\sigma$  errors. This is to be expected of simple compounds and ideal gas formulations. It also results from the fact that each group is using very similar literature. This indicates that the data garnered using molten calcium salts will be reasonably independent of the choice of data set. Deviations from ideal behavior will be similar for each data set as nonideal behavior is referenced to  $RT \ln X$  terms ( $X$  = mole fraction,  $R$  = gas constant,  $T$  = temperature kelvin). Data for the phosphates are not available for comparison.

#### Data sources

Two methods are used for determination of the liquidus positions used in this paper. The first is the quench method, outlined above, and the second is differential thermal analysis (DTA). In the DTA studies, reversals are conducted during repeated heating and cooling cycles. This method is commonly used in the calibration of thermocouples vs. a known melting point, such as that of sodium chloride.

WENTZ et al. (1969) and REUTOVA and LUKASHENKO (1971) presented liquidus temperatures derived from differential thermal analysis (DTA) studies for the join CaF<sub>2</sub>-CaCl<sub>2</sub>. Good agreement was found for the CaCl<sub>2</sub> and CaClF liquidus surfaces, but some disagreement was apparent in the CaF<sub>2</sub> liquidus surface (Fig. 1). There are also slight differences in the position of the peritectic, but careful reading of the WENTZ et al. (1969) data shows that their data are consistent with the peritectic position of REUTOVA and LUKASHENKO (1971). Both fluorite liquidus were treated equally as "reversals" of the CaF<sub>2</sub> liquidus, because neither study was clearly in error.

The apatite-salt joins are formally a portion of the whitlockite (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>)-salt systems. The whitlockite-apatite joins are generally out of the reach of most experimental equipment, due to the high melting points of whitlockite (1810°C, BERAK, 1961; BERAK and TOMCZAK-HUDYMA, 1972) and apatites (BERAK, 1972; BERAK and TOMCZAK-HUDYMA, 1972). The lower temperature portions of these binary subsystems have been studied by MORTON (1961) and EPPERLEIN and LEHMANN (1973, 1975; Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-CaCl<sub>2</sub>), BIGGAR (1966; Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-Ca(OH)<sub>2</sub>), and BERAK (1961) and BERAK and TOMCZAK-HUDYMA (1972; Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-CaF<sub>2</sub>).

Central to the concept of phase equilibria is the assumption that there is a melting point for the pure substance. For the apatites the concept of melting point becomes obscure, because the apatites in an open environment do not melt, but disproportionate. At high temperatures in open systems, the apatites lose halogens and water (MORTON, 1961; PRENER, 1967, 1971; PRENER et al., 1969; BERAK and TOMCZAK-HUDYMA, 1972; SKINNER et al., 1975; ARENDS et al., 1987). The open system products are oxyapatites (MORTON, 1961; TROMBE and MONTEL, 1978) or admixtures of the apatite and whitlockite (SKINNER et al., 1975). At temperatures above 1050°C oxyapatite breaks down to mixtures of whitlockite and tetracalcium phosphates (TROMBE and MONTEL, 1978). Melting points have been measured for the endmember apatites (BHATNAGAR, 1969), but it is likely that these temperatures do not reflect melting of the pure substance. It is significant that the melting point measured for FAp by BHATNAGAR (1969) is the same as the eutectic temperature between whitlockite and fluorapatite given by BERAK (1961) and BERAK and TOMCZAK-HUDYMA (1972), suggesting that CaF<sub>2</sub> was lost during heating. This is a mechanism identical to the high-temperature loss of CaCl<sub>2</sub> from ClAp in vacuum identified by PRENER (1971).

For these reasons, the data of MORTON (1961) on the join ClAp-CaCl<sub>2</sub> were not used in this study. MORTON (1961) used open containers, which resulted in a loss of material during the experiments at temperatures above 1200°C, as was noted by the author. Good agreement is found for the position of the Ca<sub>2</sub>PO<sub>4</sub>Cl-CaCl<sub>2</sub> eutectic in the studies of MORTON (1961) and EPPERLEIN and LEHMANN (1973, 1975). Incongruent melting of Ca<sub>2</sub>PO<sub>4</sub>Cl to ClAp and CaCl<sub>2</sub> was found to be at 945°C  $\pm$  5° by MORTON (1961) and 1030°C by EPPERLEIN and LEHMANN (1973, 1975; Fig. 2a). In our own synthesis of ClAp in sealed capsules, chlosporodisite is the stable phase at 1000°C.

BERAK and TOMCZAK-HUDYMA (1972) presented DTA data for the entire system Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>-CaF<sub>2</sub> up to the melting point of FAp

and whitlockite (Fig. 2b). A new phase was identified as Ca<sub>7</sub>(PO<sub>4</sub>)<sub>4</sub>F<sub>2</sub>, dubbed Apatite B to distinguish it from the more familiar apatite they called Apatite A. Later results showed that the new Apatite B did not occur (J. BERAK, pers. commun., 1991). The data of BERAK and TOMCZAK-HUDYMA (1972) were used with some corrections. The FAp melting point is accepted with the assumption that the experiments took place rapidly enough to preclude significant disproportionation of the apatite. The eutectic positions and temperatures were accepted as correct, because these are points that are repeatedly measured during DTA experiments. The fluorite liquidus was correct, but use of these data points in the absence of FAp liquidus points significantly biased the statistical model. An initial condition in these experiments is that they take place at high ratios of salt to phosphate. This means that bulk compositions between the ternary eutectic and the binary will be in the fluorite + liquid field. Knowledge of the effects of fluorite on the FAp liquidus is therefore superfluous to the present study, but were they determined for future use in the ternary systems and for comparison to other phosphate-salt systems.

BIGGAR (1966) presented a small amount of data on the join HAp-Ca(OH)<sub>2</sub>, limited by the thermal stability of cold-seal pressure vessels (Fig. 2c). This pseudobinary is rather remarkable in that the melting point of Ca(OH)<sub>2</sub> drops 70°C with the addition of only 1 mol% Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, to the eutectic at 765°C and 99 mol% Ca(OH)<sub>2</sub>. The possibility of some error existed, but our own experiments on the anhydrous melting of Ca(OH)<sub>2</sub> confirm the results of WYLLIE and TUTTLE (1959). The position of the eutectic has been confirmed (ROY, 1971; EYSEL and ROY, 1973; ROY et al., 1978). Hence, the extreme drop in the portlandite liquidus is real and not an artifact of experimental procedure.

#### Thermodynamic models

The mathematical methods followed here have been discussed in detail by THOMPSON (1967), BERMAN and BROWN (1987), NAVROTSKY (1987), TACKER and STORMER (1989), and in TACKER (1992). Binary interaction coefficients,  $W_G$ 's, are calculated for pairs of components from phase equilibrium data, where  $W_G = W_H - TW_S$ .  $W_G$  is the binary free energy interaction coefficient,  $W_H$  and  $W_S$  binary enthalpy and entropy interaction coefficients, and  $T$  temperature kelvin.

Calculation methods are discussed more thoroughly in TACKER (1992). Briefly, binary interaction coefficients were found by least-squares regression methods, using the experimental brackets of the liquidus. For example, a solution model is determined for the reaction  $\text{CaCl}_2^{\text{sl}} = 2 \text{Ca}_{0.5}\text{Cl}^{\text{melt}}$ . At equilibrium,  $\Delta G_{(T,P)\text{reaction}} + 2 RT \ln (a_{\text{Ca}_{0.5}\text{Cl}^{\text{melt}}}) = 0$ , where  $\Delta G_{(T,P)}$  is the Gibbs Free Energy of the reaction at the temperature and pressure of interest,  $R$  is the gas constant,  $T$  is temperature kelvin, and  $a$  is activity. Noting that  $a_{\text{Ca}_{0.5}\text{Cl}^{\text{melt}}} = (X_{\text{Ca}_{0.5}\text{Cl}^{\text{melt}}})(\gamma_{\text{Ca}_{0.5}\text{Cl}^{\text{melt}}})$ , where  $X$  is mole fraction and  $\gamma$  is the activity coefficient, the nonideal contribution to activity.

A hierarchy of models is available to describe the deviation from ideal mixing for a liquid. For example, in asymmetric solutions, the deviations from ideal mixing are a function of composition and  $RT \ln(\gamma_i^{\text{melt}}) = (W_G)_{\text{H,F}}(X_i^2(1 - 2X_{\text{H}})) + (W_G)_{\text{F,H}}(2X_i^2X_{\text{H}})$ .  $(W_G)_{\text{H,F}}$  is the binary Gibbs Free Energy interaction coefficient for hydrophyllite in a fluorite-bearing melt. (Melt components will hereafter be abbreviated as subscripts P, F, H, and W for portlandite, fluorite, hydrophyllite, and whitlockite, respectively.) In the simplest case of a regular solution where  $W_G$  is independent of temperature,  $(W_G)_{\text{H,F}} = (W_G)_{\text{F,H}} = (W_H)_{\text{H,F}}$  where  $W_H$  is the binary enthalpy interaction parameter. If  $W_G$  is a function of both composition and temperature,  $W_G = W_H - TW_S$ , and  $W_S$  is the entropy interaction parameter. In an asymmetric regular solution,  $(W_G)_{\text{H,F}} \neq (W_G)_{\text{F,H}}$ . Again,  $W_G$  may be a function of temperature. The hierarchy of models of increasing complexity is then regular solution, symmetric solution with  $W_S$  terms, asymmetric solution without  $W_S$  terms, and asymmetric solution with  $W_S$  terms. The approach adopted here is that the simplest model required to reproduce the original data was the best.

Configurational entropy of the melt was expressed as molten CaCl<sub>2</sub>, and as single-anion component such as Ca<sub>0.5</sub>Cl. The second expression is essentially the Temkin hypothesis (TEMKIN, 1945; KLEPPA, 1977, 1987). Both expressions were tested in modeling the system CaCl<sub>2</sub>-CaF<sub>2</sub>, for which standard state data were available for the molten

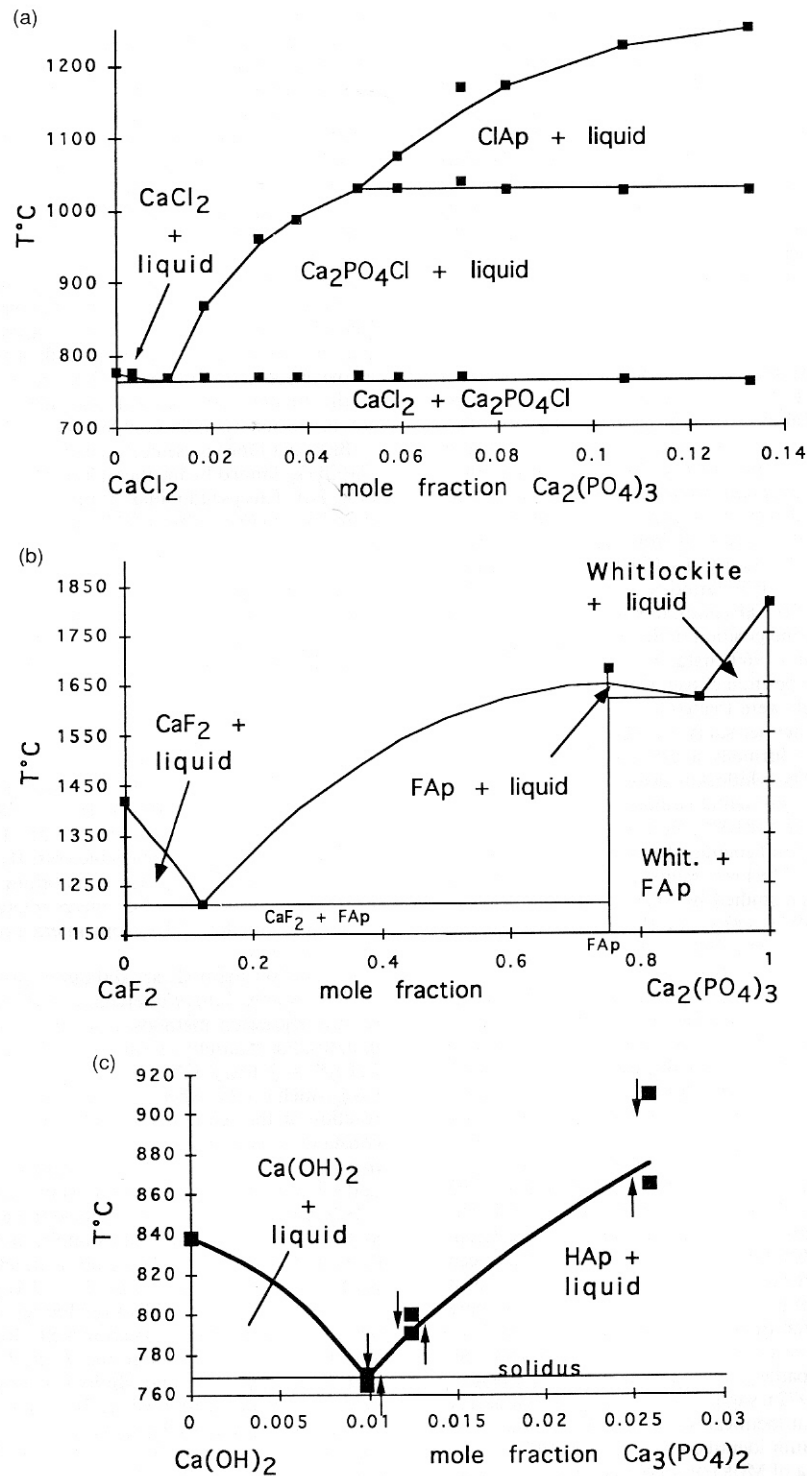


FIG. 2. Experimental data for the calcium salt-whitlockite joins. In all diagrams, the solid line is the calculated liquidus. (a)  $\text{Ca}_3(\text{PO}_4)_2$ - $\text{CaCl}_2$  (EPERLEIN and LEHMANN, 1973, 1975) at 1 bar. (b) The system  $\text{Ca}_3(\text{PO}_4)_2$ - $\text{CaF}_2$  (BERAK and TOMCZAK-HUDYMA, 1972) at 1 bar. (c) The system  $\text{Ca}(\text{OH})_2$ -HAp at 1 kbar pressure, from the data of BIGGAR (1967).

state. Standard state enthalpy and entropy were derived for the molten salts using constant heat capacities (JANAF, CHASE et al., 1985) and compared with JANAF data, which was recalculated as noted above. The  $\text{Ca}_{0.5}\text{X}$  model compared very well to the recalculated JANAF

data for the molten salts (Table 1). These derived data were used in the remainder of the modeling.

No such simple expression comes readily to hand for the phosphate systems. Phosphate is a network former akin to silicate and may

form extensive polymers. The systems under examination here are not glass-forming, as they have high concentrations of network-modifying agents. A stoichiometric model (BERMAN and BROWN, 1987) was selected in which the phosphate system component was expressed as  $\text{Ca}_{1.5}\text{PO}_4$ .

In determination of molten salt standard state data, experimental data were weighted to better reproduce melting points. Linear least squares regression is dependent on the arithmetic means of  $x$  and  $y$  (EDWARDS, 1979), so that weighting of an end point shifts the mean closer to the melting point. The net result is that the melting point is met more closely. For these derivations, the melting point of fluorite was weighted ten times, and that of portlandite five times. While it might be considered that a higher order heat capacity function would be preferable to the tactic of weighting the data, higher order heat capacities tended to result in unacceptable signs for enthalpies or entropies of formation.

Several essential pieces of information are missing for the quaternary system:  $\Delta H_{\text{fusion}}$  for  $\text{Ca}(\text{OH})_2$ ,  $\text{Ca}_2\text{PO}_4\text{Cl}$ ,  $\text{CaClF}$ ,  $\text{CaClOH}$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , and for all the apatite endmembers;  $\Delta G^0$  for molten  $\text{Ca}(\text{OH})_2$ , molten  $\text{Ca}_3(\text{PO}_4)_2$  (or  $\text{Ca}_{1.5}\text{PO}_4$ ) and for crystalline  $\text{Ca}_2\text{PO}_4\text{Cl}$ ,  $\text{CaClF}$ , and  $\text{CaClOH}$ ; and  $\Delta V$  ( $V$  = molar volume) for fusion reactions of the for the phosphates and for  $\text{Ca}(\text{OH})_2$ . The molar volume of fusion for  $\text{Ca}(\text{OH})_2$  liquid is incorporated into its standard state enthalpy. Hence, these molten  $\text{Ca}(\text{OH})_2$  data are best suited for use only at 1 kbar.

#### Derivation of expressions for $\text{Ca}_{0.5}\text{OH}^{\text{melt}}$ and $\text{Ca}_{1.5}\text{PO}_4^{\text{melt}}$

Strategies for determination of standard state data for the unknown liquids incorporate the increasing complexity of the hierarchy of models discussed above. An ideal solution model allows calculation of the liquid properties directly from the liquidus data. A regular solution model, and a symmetric solution model may all be imposed upon a data set, if the standard state data for the other liquidus of the binary system are known. For these determinations, liquid heat capacities were assumed to be constant (CHASE et al., 1985). Higher order heat capacity equations were attempted, but rapidly lead to unacceptable sign for standard state entropy or enthalpy. Success was measured not by statistical measures but by the ability of the model to reproduce the original data.

Initial attempts to produce standard state data for the liquid  $\text{Ca}(\text{OH})_2$ , using the protocol given above, were unsuccessful. During initial attempts to model the two  $\text{Ca}(\text{OH})_2$ -bearing systems, it became

clear that symmetric models were not sufficient to reproduce the data, but that an asymmetric regular solution model worked well on both. Therefore, both thermodynamic models and standard state data were iteratively optimised. The starting expression for molten  $\text{Ca}(\text{OH})_2$  was taken from the  $\text{Ca}(\text{OH})_2$ - $\text{CaCl}_2$  system, with the melting point weighted five times. Asymmetric regular solution models were calculated for both systems with this expression and the intercepts reduced as much as possible by moving the liquidus point within the brackets. Then new standard state for molten  $\text{Ca}(\text{OH})_2$  were calculated. Heat capacity converged after two iterations and was not further refined as it compared well with that estimated in CODATA (GARVIN et al., 1987) by other methods. Two further iterations were required before converging upon the final model.

Initial attempts to determine  $\Delta G^0$  for  $\text{Ca}_{1.5}\text{PO}_4$  with an ideal model were promising (Fig. 3). An estimate was made from the apatite liquidus data of EPPERLEIN and LEHMANN (1973, 1975), BIGGAR (1966), and BERAK and TOMCZAK-HUDYMA (1972), for example, by the reaction  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}^{\text{apatite}} = 3\text{Ca}_{1.5}\text{PO}_4^{\text{melt}} + \text{Ca}_{0.5}\text{Cl}^{\text{melt}}$ . This is shown in Fig. 3 as  $\Delta G_{T,P}$  vs. temperature kelvin. For this representation, slope is equal to the negative of  $S^0$  and intercept equal to  $H^0$ . The close agreement of the calculated data indicates that the basic thermodynamic data for the apatites are quite good. Note that the slopes are roughly equivalent. Although the differences in slope are small, they are significant. Regression of the data calculated from all four liquidus gives an expression that intersects each line at a small angle, which results in both positive and negative deviations from ideal mixing within each separate system, when applied to the original data. These three lines do not overlap due to possible nonideal terms and differences in pressure of the experiments. To a first approximation, pressure terms are assumed to be small in comparison to other terms.

When imposition of the regular solution and symmetric solution models failed to produce an acceptable answer, an expression for the standard state of molten  $\text{Ca}_{1.5}\text{PO}_4$  was derived from the whitlockite liquidus (BERAK and TOMCZAK-HUDYMA, 1972). Enthalpy of fusion ( $\Delta H_{\text{fus}}$ ) estimated from the two points on the whitlockite liquidus using the relation

$$\Delta H_{\text{fus}} = \frac{R \ln a}{(1/T - 1/T_{\text{fusion}})}$$

(SABOUNGI and CERISIER, 1974). These data are limited in temperature range, but the limited compositional range means that the non-

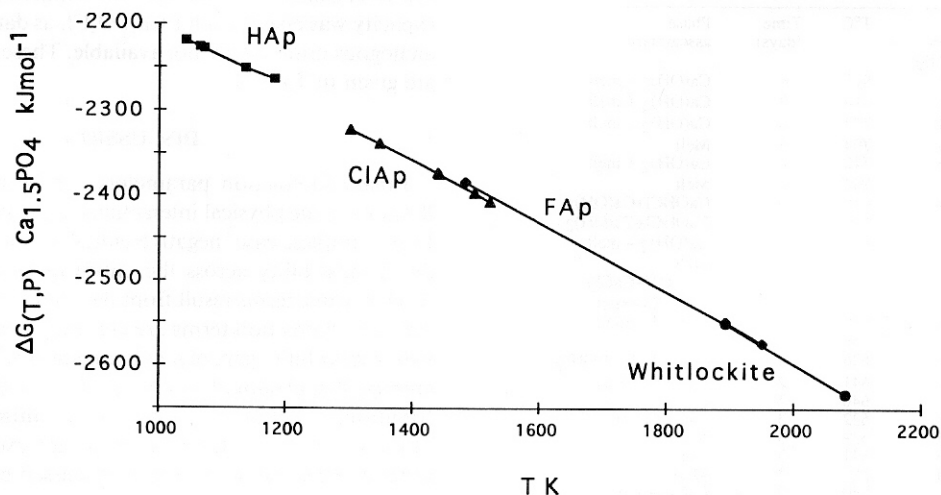


FIG. 3.  $\Delta G$  at temperature and pressure for molten  $\text{Ca}_{1.5}\text{PO}_4$ , calculated from the apatite and whitlockite liquidus surfaces using an ideal model. Source, slopes, and intercepts for the lines are HAp (BIGGAR, 1967):  $-0.335$  and  $-1868.657$   $\text{kJ mol}^{-1}$ ; ClAp (EPPERLEIN and LEHMANN, 1973, 1975):  $-0.382$  and  $-1825.233$ ; FAp (BERAK and TOMCZAK-HUDYMA, 1972):  $-0.402$  and  $-1788.0068$ ; whitlockite:  $-0.432$  and  $-1733.735$ . Slope equals negative  $S^0$ , intercept equals  $\Delta H^0$ . Initial agreement among the three data sources at these temperatures indicates that the apatite standard state data and the experimental data are quite good. However, the differences in slope suggest significant deviations from ideal mixing within each system.

ideal terms are negligible. The expression for  $\Delta G^0$  for molten  $\text{Ca}_{1.5}\text{PO}_4$  was iterated with the thermodynamic model for  $\text{Ca}_3(\text{PO}_4)_2\text{-CaF}_2$ . This allowed the calculation of  $\Delta H_{\text{fus}}$  for FAp. This enthalpy of fusion for the other apatites was assumed to equal that of fluorapatite.

## RESULTS

### Experimental Results

Experimental results are given in Tables 2 and 3, and shown in Fig. 1a and b. Our experiments on the melting of pure portlandite under water-free conditions confirm the results of WYLLIE and TUTTLE (1959), who place the melting point at 835°C. The liquidus determined in the system  $\text{CaF}_2\text{-Ca(OH)}_2$  is somewhat higher than that of GITTINS and TUTTLE (1964). The differences can be attributed to the differences in run duration. The experiments of GITTINS and TUTTLE (1964) lasted only fifteen minutes, while the experiments presented here lasted far longer, and grew larger crystals of portlandite. The differences in size of the crystals probably made identification of crystal-present conditions easier.

The system  $\text{CaCl}_2\text{-Ca(OH)}_2$  is not as simple as  $\text{CaF}_2\text{-Ca(OH)}_2$ , as it has an intermediate compound  $\text{CaClOH}$ . This compound melts congruently at about 744°C and 1 kbar pressure. There are two eutectics in the system, unlike the other molten salt joins, which contain only one eutectic, or one eutectic and a peritectic.

### Results of Thermodynamic Modeling

Results of the model are given in Tables 1, 2, and 3 and shown in Fig. 1 and 2. Model parameters are given in Table 4. The calculated liquidus temperatures are shown in Fig. 1 and 2.

**Table 2.** Definitive experiments in the system  $\text{CaCl}_2\text{-Ca(OH)}_2$  at one kilobar pressure.

Composition Weight fraction $\text{CaCl}_2$ $\text{Ca(OH)}_2$		T°C	Time (days)	Phase assemblage
0.09	0.91	812	6	$\text{Ca(OH)}_2$ + melt
0.09	0.91	816	3	$\text{Ca(OH)}_2$ + melt
0.22	0.78	777	3	$\text{Ca(OH)}_2$ + melt
0.22	0.78	794	3	Melt
0.30	0.70	742	4	$\text{Ca(OH)}_2$ + melt
0.30	0.70	744	6	Melt
0.40	0.60	635	5	$\text{CaOHCl} + \text{Ca(OH)}_2$
0.40	0.60	640	11	$\text{CaOHCl} + \text{Ca(OH)}_2$
0.49	0.51	657	4	$\text{Ca(OH)}_2$ + melt
0.49	0.51	665	4	Melt
0.57	0.43	613	3	$\text{CaClOH} + \text{CaCl}_2$
0.57	0.43	621	6	$\text{CaClOH} + \text{melt}$
0.57	0.43	639	2	$\text{CaClOH} + \text{melt}$
0.57	0.43	646	3	Melt
0.59	0.41	626	4	$\text{CaClOH} + \text{Ca(OH)}_2$
0.59	0.41	641	2	$\text{CaClOH} + \text{melt}$
0.59	0.41	646	3	Melt
0.65	0.35	632	3	$\text{CaClOH} + \text{melt}$
0.65	0.35	639	3	Melt
0.70	0.30	621	3	$\text{CaClOH} + \text{melt}$
0.70	0.30	627	3	Melt
0.80	0.20	640	3	$\text{CaCl}_2$ + melt
0.80	0.20	649	3	Melt
0.91	0.09	615	3	$\text{CaCl}_2 + \text{CaClOH}$
0.91	0.09	683	3	$\text{CaCl}_2$ + melt
0.91	0.09	693	3	$\text{CaCl}_2$ + melt
0.91	0.09	715	6	Melt
0.56	0.44	640-646		Eutectic
0.74	0.26	615-617		Eutectic

**Table 3.** Definitive experimental results on the  $\text{Ca(OH)}_2$  liquidus in the system  $\text{Ca(OH)}_2\text{-CaF}_2$ .

Composition Weight fraction $\text{Ca(OH)}_2$ $\text{CaF}_2$		T°C	Time (days)	Phases present
0.95	0.05	760	6	$\text{Ca(OH)}_2$ + melt
0.95	0.05	800	6	$\text{Ca(OH)}_2$ + melt
0.95	0.05	812	6	Melt
0.85	0.15	760	6	$\text{Ca(OH)}_2$ + melt
0.85	0.15	763	7	$\text{Ca(OH)}_2$ + melt
0.85	0.15	767	5	$\text{Ca(OH)}_2$ + melt
0.85	0.15	771	3	Melt
0.75	0.25	760	6	Melt
0.75	0.25	711	5	$\text{Ca(OH)}_2$ + melt
0.75	0.25	715	6	Melt

The results for the  $\text{CaCl}_2\text{-CaF}_2$  system reflect ideal mixing between the two melt components. It might be expected that  $\text{OH}^-$  would display similar behavior given its size and charge. When  $\text{Ca(OH)}_2$  is mixed with either of the other two salts, large positive deviations from ideal behavior are observed. This implies the presence of a miscibility gap in the system, which is not observed, although textures of one or two runs in the  $\text{CaCl}_2\text{-Ca(OH)}_2$  compositions suggest supercooling into the immiscible region.

The phosphate systems are not as complete as the salts, but they are sufficient to permit some insight into the mixing behavior of the salts and phosphates. Enthalpies of mixing parameters are negative. Entropies of mixing for the  $\text{CaCl}_2$  and  $\text{Ca(OH)}_2$  apatite melts, are also negative. This seems quite the reverse of what might be predicted, and will be discussed further in the next section.

Standard state thermodynamic data does not exist for several crystalline phases present in these systems:  $\text{CaClF}$ ,  $\text{CaClOH}$ , and  $\text{Ca}_2\text{PO}_4\text{Cl}$ . The models developed allow these to be calculated. Enthalpies of melting were estimated from the differences in solid-solid and solid-liquid reactions at invariant points. Heat capacities were estimated for  $\text{CaClF}$  and  $\text{CaClOH}$  from combination of the endmember salts. No heat capacity was estimated for  $\text{Ca}_2\text{PO}_4\text{Cl}$ , as data for structurally analogous minerals are not available. These  $\Delta H^0$  and  $S^0$  data are given in Table 1.

## DISCUSSION

Binary interaction parameters can be interpreted as reflections of the physical interactions in the systems of interest. In the simplest case, negative enthalpy interaction terms indicate miscibility across the entire range of compositions, while positive terms result from the presence of immiscibility. Entropy interaction terms are generally positive. In a system with a miscibility gap, higher temperatures lead to increasing entropy that eventually outweighs the positive enthalpy contribution, resulting in closure of the miscibility gap (NAVROTSKY, 1987). However, there are exceptions to these general expectations, as will be discussed below.

### Discussion of Molten Salt Results

In the case of  $\text{Ca(OH)}_2$  mixing with the other halogen salts, the positive enthalpy parameters are typical of mixed-anion systems and are not an artifact of the modeling procedure. KLEPPA (1977, 1987) has shown with calorimetric



**Table 4.** Thermodynamic parameters derived with the melt model discussed in the text.

System		Wh <sub>1,2</sub>	Wh <sub>2,1</sub>	Ws <sub>1,2</sub>	Ws <sub>2,1</sub>
1	2	kJ/mol	kJ/mol	J/mol·K	J/mol·K
CaCl <sub>2</sub>	CaF <sub>2</sub>	0	0	0	0
CaCl <sub>2</sub>	Ca(OH) <sub>2</sub>	7.253	8.836	0	0
		±0.653	±0.741		
CaF <sub>2</sub>	Ca(OH) <sub>2</sub>	3.952	4.728	0	0
		±0.836	±0.269		
CaCl <sub>2</sub>	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	-104.751	-160.887	-9.324	-103.242
		±18.866	±0.8221	±11.688	±0.404
CaF <sub>2</sub>	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	-2.093	-23.3670		0
		±3.142	±1.43		
Ca(OH) <sub>2</sub>	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> <sup>†</sup>	-116.8		-78.226	
		±7.52		±6.881	
Ca(OH) <sub>2</sub>	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> <sup>‡</sup>	-8484.063		3.943	
		±15899.520		±15.39	
Ca(OH) <sub>2</sub>	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> <sup>‡‡</sup>	-12557.772			
		±817.095			
Ca(OH) <sub>2</sub>	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> <sup>*</sup>	-116.8		-78.06	
		±8.707		±8.014	

Notes:

† Symmetric solution data derived in binary system only. Intercept equals -1.576 kJ/mol.

‡ Symmetric solution data derived using only portlandite liquidus in binary and ternary systems of BIGGAR (1967). Intercept equals zero.

‡‡ Regular solution data derived using only portlandite liquidus in binary and ternary systems of BIGGAR (1967). Intercept equals zero.

\* Symmetric solution data derived from HAp liquidus in binary system. Intercept equals zero.

measurements that single cation-mixed anion solutions (e.g., NaF-NaI, NaF-NaBr) tend to form asymmetric solutions showing positive deviations from ideal mixing. Such deviations occur in mixtures of CaCl<sub>2</sub> and CaBr<sub>2</sub>, where  $W_H = 1.142$  kJ/mol and  $G_{\text{excess}} = 285$  Jmol<sup>-1</sup> at 50 mol% (OSTVOLD, 1971).

KLEPPA (1977, 1987) attributes these deviations to differences in size and polarizability of the salts being mixed. As the polarizability increases, second-nearest-neighbor interactions have a larger contribution to enthalpies of mixing, attributed to London-van der Waals dispersion. While coulombic interactions have negative contributions to the enthalpy of mixing, the London-van der Waals interactions have positive contributions.

Anion size difference alone is insufficient to account for the differences in free energy of mixing measured here. The data of SHANNON (1976) show that the differences in anion size are Br-Cl, 0.15 Å; OH-F, 0.04 Å; Cl-OH, 0.44 Å; and Cl-F, 0.48 Å. It is clear from our results that the introduction of a hydroxide dipole into the polarizable mixture leads to small asymmetric positive mixing terms, and the comparative magnitudes of excess free energy are consistent with differences in anion size for our results. These trends are not consistent with data obtained at 1 bar and it appears that differences in pressure preclude direct comparisons.

In general, comparison of the derived thermodynamic data for the intermediate compounds Ca<sub>2</sub>PO<sub>4</sub>Cl, CaClF, and CaClOH with other sources is not possible. HISHAM and BENSON (1987) showed that estimation of enthalpies of formation by simple additive relationships tends to give answers that were less negative than the measured enthalpies. In the case of CaClF, the enthalpy determined from the endmembers is -1012.53 kJ/mol while our value, -1020.465 kJ/mol, is more negative. The model enthalpy for CaClOH is -852.714 kJ/mol, less negative than the additive value of -890.943.

On the other hand, the derived enthalpy of melting for Ca(OH)<sub>2</sub>, ~25 kJ/bar at 1 kbar pressure, agrees very well with that estimated in the CODATA tables, 29 kJ/bar at one bar. This is also true of the calculated heat capacity for molten Ca(OH)<sub>2</sub>, 175.876 J/mol as compared to 153 J/mol in CODATA.

### Discussion of Phosphate-Salt Mixing Results

Model parameters for phosphate-salt binaries are given in Table 4. They illustrate a basic problem in the use of buffers: some interaction between buffers and reactants may occur. In this case, the deviations from ideality are significant and demonstrate that the assumption of ideal mixing behavior can introduce error into the thermodynamic analysis of the experiments. Another problem lies in that complete data may not be available for the refractory mineral-salt binary.

The results for the HAp-Ca(OH)<sub>2</sub> join are complicated by the extreme drop in the Ca(OH)<sub>2</sub> liquidus. There are essentially five points in this system: three for the HAp liquidus, the eutectic, and the melting point of portlandite. On the Ca(OH)<sub>2</sub>-HAp join, the liquidus temperatures for portlandite from 99-100 mol% are not closely met, although the HAp liquidus is reproduced well.

The reasons for this are most easily explained using a regular solution example. More complex models will have more parameters, but similar topologies. Let  $\Delta G_{\text{xs}}$  (excess  $\Delta G$  of mixing for the liquid, calculated from the fusion reaction) equal  $RT \ln \gamma$  terms. For the portlandite liquidus

$$(W_G)_{\text{WP}} = \frac{X_W^2}{\Delta G_{\text{XS}}}$$

The eutectic lies at 99 mol% Ca(OH)<sub>2</sub>, so the  $X_W^2$  term becomes very small for the portlandite liquidus (0.0002 at the eutectic and decreasing as the endmember is approached),

and  $W_G$  becomes proportionally larger. For the intermediate compound HAp, the equilibrium constant for the fusion reaction is a combination of the endmember terms and

$$(W_G)_{WP} = \frac{X_W^2 + 3X_P^2}{\Delta G_{XS}}$$

In  $\Delta G_{XS}$  vs.  $X^2$  space, these points are widely separated, as  $\Delta G_{XS}$  for HAp fusion is on the order of  $-100 \text{ kJ mol}^{-1}$  at the eutectic. Any fit of the data is biased in favor of the points far from the origin, in this case,  $\Delta G_{XS}$  for HAp. The regression for this line must pass through the origin, which is  $\Delta G_{\text{excess}}$  for the melting of the pure substances. This will not happen because the precipitous drop in portlandite liquidus temperature at 99 mol%  $\text{Ca}(\text{OH})_2$  gives a point at  $y(\Delta G_{\text{excess}}) = -2.46 \text{ kJ mol}^{-1}$  and  $x = 0.0002$ . Additional data points on the HAp liquidus would improve the situation somewhat by giving points closer to the origin, but these points will not improve the fit of any model to the data near the origin.

Use of a higher order thermodynamic model will not solve the problem, because the model will again be biased in favor of the points derived from the hydroxylapatite liquidus and the requirement to include the origin. The choices at this point are to fit the liquidus separately, or accept the fact that intercepts for the entire data set will not equal zero. If intercepts are used, then the melting curve near the melting point is not reproduced well. Both of these solutions are given in Table 4. For the portlandite liquidus, we included the ternary eutectic of BIGGAR (1967). Comparison of the different results in Table 4 shows the degree to which the model is biased in favor of the HAp data, as well as the degree of nonideality for the melting of portlandite in the presence of a phosphate.

The data for the FAp- $\text{CaF}_2$  portion of this system, melting points and eutectic, are described well with an asymmetric regular solution model. The fluorite liquid component behaves nearly ideally when mixed with the phosphate, as  $W_{HF,W}$  is equal to zero within error. The only portion of the system not approximated by this model is the melting point of FAp, which is underestimated by about fifteen degrees. However, this is a minor problem. The FAp- $\text{CaF}_2$  eutectic and the solidus in this system are the two points that are measured most often during DTA. This is the essential portion of the system, as the initial premise in this study is the use of molten salts at low phosphate concentrations.

The data for the ClAp- $\text{CaCl}_2$  join are the most complete of any of the apatite-salt joins. Reproduction of this data set requires a full four-parameter mixing model. The original data and the curvature of the ClAp liquidus cannot be reproduced without negative entropy of mixing terms. The appearance of the sign reversals in the entropy terms alone indicates a possible complexities arising from the configurational entropy model chosen.

### The Structure of Phosphate Melts

The model results for the phosphate systems may be better understood through examination of data available for the phosphate glasses. The modeled systems do not quench to glass because too many flux-like network-modifying components are present. However, spectroscopic and chromatographic investigations of phosphate glasses can yield some

insight into the nature of phosphate-water and phosphate-halogen species that may be present in these less polymerized compositions.

The basic unit of phosphate glasses is a  $-\text{PO}_4$  tetrahedron (WESTMAN, 1977; MATSUBURU et al., 1988; MATZ et al., 1988). Similarities exist between phosphate glasses and silicate glasses, particularly in the nature of polymerization, but the key difference between the two lies in the 5+ charge on the phosphate. Another is the ease with which phosphate glasses can be dissolved, making them easily analysed by chromatography (WESTMAN, 1977; MASSON, 1990). In pure phosphate polymers, one of the oxygens is double-bonded to the phosphate, although "the double bond character may be smeared over all four bonds to a considerable extent" (WESTMAN, 1977). Addition of F to the glass results in the formation of  $\text{PO}_3\text{F}$  groups (SAMMET and BRUCKNER, 1985, 1987; KOULDEKA et al., 1986; VIDEAU et al., 1982; MURTHY and MUELLER, 1963; MURTHY, 1963). Fluorine causes a delocalization of the double bond such that only bridging and nonbridging oxygens remain in the polyhedra (SAMMET and BRUCKNER, 1987). Water, present as hydroxide groups, plays much the same role (DAY and STEVELS, 1974; ABE, 1983). Differences occur in that fluorine is initially a network-forming component (SAMMET and BRUCKNER, 1985, 1987), water has the only opposite effect (DAY and STEVELS, 1974; ABE, 1983).

If Ca is added to a pure phosphate glass, it behaves as a network modifier (BOBOVICH, 1962; SAMMET and BRUCKNER, 1987; ABE, 1983; MATSUBARA et al., 1988; MATZ et al., 1988). Research summarized by ABE (1983) shows that the addition of Ca shortens the length of the average phosphate chain. In glasses of 3:1  $\text{CaO}:\text{P}_2\text{O}_5$  composition equivalent to whitlockite stoichiometry, glasses are almost entirely orthophosphate ( $\text{Ca}_{1.5}\text{PO}_4$  or  $\text{Ca}_3(\text{PO}_4)_2$ ) and pyrophosphate ( $\text{Ca}_2\text{P}_2\text{O}_7$ ) groups (ABE, 1983).

With these results in mind, the combination of whitlockite with a hydroxide- or a halogen-bearing calcium salt is qualitatively predictable. The phosphate network will be increasingly modified and shortened by reaction between the phosphate groups and the salt. This explains the negative entropy of mixing terms found for the ClAp- $\text{CaCl}_2$  and HAp- $\text{Ca}(\text{OH})_2$  systems: The choice of melt components implicitly assumes random mixing of  $\text{Ca}_{0.5}X$  ( $X = \text{F}, \text{Cl}, \text{OH}$ ) and  $\text{Ca}_{1.5}\text{PO}_4$ . The actual reactions that take place in the melt are less random than this, and probably result in halogenated or hydroxylated orthophosphate and/or pyrophosphate groups. While our choice of system components and statement of configurational entropy are satisfactory for thermodynamic description of these systems, it is less adequate for physical description of the melt species. Therefore, the negative entropy interaction parameters are an artifact of our selection of phosphate melt components, and an indication of ordering in the melt. The presence of negative entropy interaction parameters does not diminish the ability of the model to describe the melt-crystal relationships.

The spectroscopic data also explain the precipitous drop in the portlandite liquidus. Phosphate glasses, and phosphates in general, are extremely hygroscopic (DAY and STEVELS, 1974; ABE, 1983). The presence of phosphate does not strongly affect the liquidus of  $\text{CaCl}_2$  or  $\text{CaF}_2$ , because the

salts do not dissolve much phosphate. Portlandite, however, must react with the phosphate. Although the portlandite melt soon reaches saturation with an apatite (BIGGAR, 1967), the nature of the phosphate dissolved in the portlandite melt must be different than that in the  $\text{CaCl}_2$  and  $\text{CaF}_2$  systems, where in liquidus temperatures do not drop as steeply in response to phosphate.

Alternative choices of melt components might eliminate the negative entropy interaction parameters. A specific melt speciation model may be imposed upon the data and resulting thermodynamic parameters derived. Alternatively, several melt species may be defined and the equilibria among them examined. In both cases, increasing complexity of the melt model proliferates the number of variables to the point where they are no longer fully constrained. At this point options are very limited. Assumptions of ideality must be introduced to the model, which we find to be unsatisfactory. Independent data on melt structure may be used, but unambiguous data do not exist for compositions in this system. In the final analysis, we choose to keep the stoichiometric melt model which gives us results that can be explained and understood in general physical terms, rather than impose an arbitrary melt speciation model upon the data in the absence of clear constraints.

To better understand the implications of the model for the ternary systems, it is helpful to examine the ternary system of BIGGAR (1967). In the  $\text{Ca}_3(\text{PO}_4)_2$ - $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$  system it is quite clear that a molten salt dissolves very little phosphate (BIGGAR (1967)). In the ternary system, the  $\text{CaF}_2$ -apatite eutectic projects to lower phosphate concentrations, to the ternary eutectic at 76 mol%  $\text{Ca}(\text{OH})_2$ , 24 mol%  $\text{CaF}_2$ , and 1 mol%  $\text{Ca}_3(\text{PO}_4)_2$ . Isocompositional sections show that at temperatures below 800°C, liquids are very close to the compositions limited by the coexistence of an apatite and a crystalline salt (BIGGAR, 1967). Only along the  $\text{CaF}_2$ -apatite co-tectic is appreciable phosphate dissolved in the melt, and only at temperatures greater than 900–1000°C. Analogous results may be expected in the ternary systems containing  $\text{CaCl}_2$ , because the  $\text{CaCl}_2$ -ClAp eutectic lies at very low phosphate concentrations (1 mol%  $\text{Ca}_3(\text{PO}_4)_2$ ). The ternary diagram will be more complex because of the presence of intermediate compounds  $\text{CaClF}$  and  $\text{Ca}_2\text{PO}_4\text{Cl}$ , but preliminary calculations shows that the stability of these phases in the ternary system is limited. The presence of these phases does not enhance the solubility of phosphate in the molten salts. The model allows calculation of the equilibrium constant for a mixed apatite at any composition in the ternary, given the assumption that ternary effects do not exist. It is clear from these that the solubility of the apatite in the molten salt is minimal. It is clear that phosphate melts containing molten salts are extremely nonideal. However, it is also clear that the presence of molten phosphate does not strongly affect the activities of the molten salts except in the case of  $\text{Ca}(\text{OH})_2$ . Although this effect is large, it is perfectly linear with respect to the square of  $X_W$ .

These observations are helpful in designing experiments in the ternary systems. The problems with the introduction of phosphate into the molten salts may be minimized by conducting experiments at low phosphate concentrations. This presents no difficulty, as it was the original premise of

this method. Another way is to conduct experiments at temperatures below the point at which significant apatite is dissolved in the melt, which coincides with the thermal limits of cold-seal pressure vessels. Data in the ternary system will also provide a means to check the model derived from the binary systems, once compositional analysis of the apatites eliminates a degree of freedom.

There are many situations where molten salts may be used in examination of anionic or cationic exchange in minerals of geologic interest. While solution properties are well understood for the salt mixture, the remaining salt-mineral joins (e.g.  $\text{KCl-KAlSi}_3\text{O}_8$ ) may not be as well constrained. The results of this study should caution against the assumption that this information is irrelevant. Recall that the effect of only 1 mol%  $\text{Ca}_3(\text{PO}_4)_2$  is to lower the melting point of portlandite 70°C. It is interesting to note that albite- $\text{NaCl}$  (KOSTER VAN GROOS and WYLLIE, 1969) and nepheline- $\text{NaF}$  (KOGARKO and KRIGMAN, 1970) mixtures display immiscibility.

Large deviations from ideal behavior may be a general feature of systems in which a high-melting-point mineral is mixed with a low-melting-point salt. Simple geometry requires that the eutectic position be below the melting point of the salt. In a simple system with only a eutectic, the greater the difference in melting points of the endmembers, the greater is the depression of the higher one's liquidus, and the closer the eutectic moves to the opposite endmember. Accompanying this depression is a greater deviation from ideality. In the join  $\text{Ca}_3(\text{PO}_4)_2$ - $\text{Ca}(\text{OH})_2$  and  $\text{Ca}_3(\text{PO}_4)_2$ - $\text{CaCl}_2$ , the eutectics lie at about 99 mol% of the salt; for  $\text{Ca}_3(\text{PO}_4)_2$ - $\text{CaF}_2$  the eutectic lies at 87 mol%. Of the three,  $\text{CaF}_2$  has the highest melting point, and the smallest deviations from ideal behavior.

Phosphate-rich melts form some of the stranger liquids observed in nature. Apatite is an essential constituent of carbonatites (HOGARTH, 1989), and is also common in magnetite-rich bodies associated with anorthosites (e.g. GEIST et al., 1990). TREIMAN (1989) proposed that mixing of phosphates with carbonates was probably nearly ideal. Data were not available to rigorously test this, and the conclusion was reached based on the evidence of other common cation-mixed anion systems. While this is a reasonable proposition, the work conducted here suggests that mixture with the phosphates will show large negative deviations from ideal behavior, and that phosphate polymerization may need to be accounted for in future models. The phosphates may present more problems than the silicates, given the presence of an extra bond available for polymerization and speciation. In the case of the magnetite-apatite liquids, it is interesting to note that phosphate glasses have a high solubility for iron: VAUGHN and KISLER (1975) synthesized glasses up to 75 mol% ( $\text{FeO} + \text{Fe}_2\text{O}_3$ ) in  $\text{P}_2\text{O}_5$ . Apatite also enhances the solubility of iron oxides in silicate melts (EPLER et al., 1986).

## CONCLUSIONS

The deviations from ideal behavior in the binary subsystems of the quaternary system  $\text{Ca}_3(\text{PO}_4)_2$ - $\text{CaCl}_2$ - $\text{CaF}_2$ - $\text{Ca}(\text{OH})_2$  can be readily modeled using binary interaction parameters. Use of a  $\text{Ca}_{0.5}X$  melt component works quite

well for molten salts of formula  $\text{Ca}X_2$ . However, a  $\text{Ca}_{1.5}\text{PO}_4$  melt component is not entirely adequate to describe the range of polymerization and speciation in halogenated phosphate melts. Unexpected results include positive deviations from ideal behavior for the  $\text{Ca}(\text{OH})_2\text{-CaCl}_2$  and  $\text{Ca}(\text{OH})_2\text{-CaF}_2$  joins, and positive entropy interaction parameters for the  $\text{Ca}_3(\text{PO}_4)_2\text{-CaCl}_2$  and  $\text{Ca}_3(\text{PO}_4)_2\text{-Ca}(\text{OH})_2$  joins. The positive enthalpy interaction parameters for the molten salt mixtures result from polarization and London-van der Waals dispersions. In the calcium orthophosphate-salt systems, the negative entropy interaction parameters are an artifact of the choice of melt components, and reflect ordering in the melt phase. This may present a challenge in future thermodynamic modeling of phosphate-bearing liquids.

Generalized conclusions of this study are as follows.

- 1) The use of molten salts as reactants offers a thermodynamically simple means to explore anionic or cationic exchange in mineral solid solutions. Most practical problems can be overcome with careful handling.
- 2) Positive deviations from Raoultian behavior may occur in the molten salt mixtures. These will generally be small, but may be thermodynamically significant.
- 3) Mixing of a high-melting point mineral with a low-melting-point salt is likely to result in large negative deviations from ideal behavior in the molten salt. This should not be ignored in thermodynamic models for salt-mineral mixtures, but the problems can be avoided through careful experiment design. This data has greatest utility in determining temperature-compositional regions where dissolution of the mineral in the salt is minimal.

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## Errata

Erratum to A. B. Cormie, H. P. Schwarcz, and J. Gray (1994) "Relation between hydrogen isotopic ratios of bone collagen and rain." *Geochimica et Cosmochimica Acta* **58**, 377–391. Two typing errors appear in Eq. 14 on p. 386, most importantly, in the C/g coefficient. The correct equation is

$$\delta D_{w\hat{y}} = -71.01 + 1.455 \cdot \delta D_b + 0.6164 \cdot RH - 0.1168 \cdot \delta D_v - 0.1960 \cdot \delta^{15}N^2 + 0.3174 \cdot C/g; n = 67, \sigma = \pm 7.6, R = 0.981. \quad (14)$$

Also four equations were incorrectly numbered in the text of paragraph 3 on p. 384:

Line 1 should read:

"Although the  $\delta D_w$  slope in Eqns. 7 and 9 is 1.0 in ac- . . ."

while line 6 should read:

". . . relation coefficients of Eqns. 6 and 7, we can determine that . . .".

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Erratum to R. C. Tacker and J. C. Stormer Jr. (1993) "Thermodynamics of mixing of liquids in the system  $Ca_3(PO_4)_2$ - $CaCl_2$ - $CaF_2$ - $Ca(OH)_2$ ." *Geochimica et Cosmochimica Acta* **57**, 4663–4676.  
 Corrections to Table 1 on page 4666:

TABLE 1

	$\Delta H^\circ$ kJ/mol	$S^\circ$ J/mol	$\Delta H_{\text{fusion}}$ kJ/mol
<i>Solids</i>			
CaClOH	-876.237	no change	no change
Ca <sub>2</sub> PO <sub>4</sub> Cl	-2261.663	449.828	22.753
<i>Liquids</i>			
Ca(OH) <sub>2</sub>	-970.321	no change	no change

The errors in Ca(OH)<sub>2</sub> and CaClOH arise from a mistake in correcting for enthalpy of fusion for portlandite. The errors in data for chlorospodosite simply were not caught in final examination of the page proofs, which reflect both a typographical error and inclusion of results of an earlier model. The conclusions are unchanged.

R. Chris Tacker

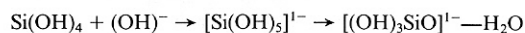
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Erratum to J. D. Kubicki, Y. Xiao, and A. C. Lasaga (1993) "Theoretical reaction pathways for the formation of  $[Si(OH)_5]^-$  and the deprotonation of orthosilicic acid in basic solution." *Geochimica et Cosmochimica Acta* **57**, 3847–3853.

### INTRODUCTION

In our original paper, we calculated the reaction pathways of the reactions



with ab initio molecular orbital calculations using a 6-31G\* basis set

(HEHRE et al., 1972). The energies of the molecular configurations were calculated at the 6-31G\* optimized geometries using an MP2/6-31G\* basis set (i.e., MP2/6-31G\*//6-31G\*). Unfortunately, the energies reported were the Hartree-Fock energies at the 6-31G\* level with the MP2 corrections (MØLLER and PLESSET, 1934; FRISCH et al., 1992). We present the intended results here for those who may try to reproduce our calculations. The differences between the original 6-31G\* and the MP2/6-31G\* results are minor, however.