

A thermodynamic model for apatite solid solutions, applicable to high-temperature geologic problems

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ABSTRACT

Experimental data of Latil and Maury (1977), Korzhinskiy (1981), and Ruzala and Kostiner (1975) on the hydroxyapatite-chlorapatite (HAp-ClAp) solid solution were modeled as symmetric and asymmetric solutions. Results of Latil and Maury (1977) and Korzhinskiy (1981) on the hydroxyapatite-fluorapatite (HAp-FAp) join were also modeled.

The regular solution model fits the HAp-ClAp data without obvious complications, yielding binary interaction parameters (W_{ij}) of less than $20 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The data suggest that the HAp-ClAp solid solution may be treated as essentially ideal at or above 500°C . Using a heat-capacity function calculated from that of FAp, the data may be reduced to give an enthalpy of formation for ClAp of $-6548.027 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and an entropy of $457 \text{ J}\cdot\text{mol}^{-1}$ at 298.15 K and 1 bar .

Data on the HAp-FAp join are not conclusive, but allow the interpretation of ideal solution. Consideration of the details of F-OH interaction support this interpretation. The presence of Na as a component in the experiments of Latil and Maury (1977) is an insurmountable obstacle to modeling their results. The reversal experiments of Korzhinskiy (1981) show that FAp essentially did not re-equilibrate at 500°C and 600°C , in agreement with the results of earlier workers. The failure of Korzhinskiy's experiments to reach equilibrium at 700°C is a useful indication of FAp behavior under hydrothermal conditions.

For all practical purposes, ClAp-HAp and HAp-FAp solid solutions may be treated as ideal at geologic temperatures and pressures.

INTRODUCTION

The fugacities of F- and Cl-bearing species are important variables in many petrologic and geochemical problems. Cl complexes are important instruments of mass transfer during metamorphism and during the formation of porphyry-type hydrothermal ore deposits. F is capable of extensive influence on the rheology (Dingwell, 1987) and phase relations (Manning, 1981; Weidner and Martin, 1987) of magmas.

Mineral indicators of the fugacities of these volatile components have not been exploited to their full potential. This is because of problems with the application of the indicators that are available. Biotites have been well-calibrated for such use (Munoz and Ludington, 1974, 1977; Munoz and Swenson, 1981). However, the ease with which biotites equilibrate in the laboratory is mirrored in nature (Stormer and Carmichael, 1971; Roegge et al., 1974; Nash, 1976; Czamanske et al., 1981). Thus they are well suited for study of hydrothermal alteration (Munoz, 1984), but may not retain their original magmatic composition in volcanic or granitic rocks. Amphiboles have not been calibrated experimentally in such detail, and the chemical complexity of amphibole solid solutions presents many (wonderful) problems for thermodynamic analysis. A further difficulty with mica and

amphibole results from the sensitivity of hydroxyl and halogen partitioning to the neighboring octahedral cations (Munoz, 1984; Volfinger et al., 1985). In addition, these mafic phases do not occur in as wide a range of environments as do apatites and are highly variable in composition across the range of environments in which they do occur. The apatites, however, present few of these problems.

A formula for apatite solid solutions can be written as $\text{Ca}_5(\text{PO}_4)_3\text{X}$, where X = F, OH, Cl, or O. Substitution of other elements for Ca and P is relatively minor in most natural samples. Apatites may be found in practically all geologic environments. It is one of the few minerals near the liquidus of both silicic and basaltic rocks (Watson, 1979, 1980; Watson and Capobianco, 1981). Chlorapatites may also be found in mantle xenoliths (O'Reilly and Griffin, 1988), mafic layered intrusions (Boudreau et al., 1986), and some meteorites (Buchwald, 1984). Apatites do not re-equilibrate under the same conditions as do biotites (Stormer and Carmichael, 1971; Roegge et al., 1974; Nash, 1976; also see below). Experimental data indicate that re-equilibration of the halogen content of apatite is sluggish below 500°C (Ekstrom, 1973) and that apatites will only partially re-equilibrate with a F-bearing fluid phase at 600°C (Latil and Maury, 1977). Even at 1300°C , end-member chlorapatite will only partially

TABLE 1. Apatite standard-state data from various sources

Reference	$\Delta H_{298.15}^0$ (kJ/mol)	$\Delta G_{298.15}^0$ (kJ/mol)	$S_{298.15}$ [J/(mol·K)]
Fluorapatite 15.7532 J/bar, $a = 9.367 \text{ \AA}$, $c = 6.884 \text{ \AA}$			
Westrich and Navrotsky (1981)	-6807.04	-6442.958	
Robie et al. (1979)	-6819.860 \pm 5	-6455.778 \pm 5	387.86
Gottschal (1958)	-6824.1	-6460.018*	
Valyashko et al. (1968)	-6825.35	-6461.268*	
Farr and Elmore (1962)	-6834.98 \pm 1.67	-6470.898*	
Smirnova et al. (1962)	-6838.74	-6474.658*	
Jacques (1963)	-6895.23	-6531.148*	
Duff (1971a)	-6740.912*	-6376.83	
Egan et al. (1951b)			387.97
Hydroxyapatite 15.8223 J/bar, $a = 9.422 \text{ \AA}$, $c = 6.883 \text{ \AA}$			
Robie et al. (1979)	-6669.259 \pm 5	-6286.093 \pm 5	390.37
Jacques (1963)	-6755.06	-6371.894*	
Gottschal (1958)	-6759.25	-6376.084*	
Smirnova et al. (1962)	-6719.5	-6336.334*	
Duff (1971a)	-6634.899*	-6251.733	
Duff (1971b)	-6640.338*	-6257.172	
Valyashko et al. (1968)	-6707.57	-6324.404*	
Chlorapatite 16.4025 J/bar, $a = 9.6418 \text{ \AA}$, $c = 6.76343 \text{ \AA}$			
Gottschal (1958)†	-6635.82		
Valyashko et al. (1968)		-6257	397.90 (est.)
Duff (1972)		-6201.52	
Vieillard and Tardy (1984)		-6223.75	
This study	-6548.027 \pm 3.335	-6201.535	457 \pm 0.023

Note: Authors' error data listed if published.

* ΔG or ΔH calculated using data of Robie et al. (1979), for the purposes of comparison.

† Quoted in Valyashko et al. (1968).

equilibrate with an H₂O-bearing gaseous phase within 2 weeks (Elliott and Young, 1967). Apatite solid solutions may also be thermodynamically simple: Korzhinskiy (1981) suggested that the apatites display nearly ideal solid solution.

This mineral group has been studied in great detail because of its importance in dentistry, biochemistry, and industry, but the available data have not been applied to high-temperature geologic problems. We have reviewed these studies and present here those applications that are relevant to high-temperature geologic problems. The mineral structure has a profound control on the mixing of the apatite end-members and will therefore be discussed first. The understanding of these structural parameters leads to specific expectations of mixing behavior, which are discussed in turn, before proceeding to discuss the thermodynamics of mixing. The thermodynamic modeling allows explicit testing for nonideal thermodynamic behavior in the solid solutions and provides the framework for interpolation and extrapolation of the experimental data.

Apatite structure

Fluorapatite (FAP) is the most familiar apatite end-member, a hexagonal mineral of space group, $P6_3/m$ (Beever and MacIntyre, 1946; Sudarsanan et al., 1972). However, hydroxyapatite (HAP) and chlorapatite (ClAp) are both monoclinic ($P2_1/b$, first setting, $\gamma = 120^\circ$, $b = 2a$) at ambient temperature and pressure (Prener, 1967; Elliott, 1971; Mackie et al., 1972; Elliott et al., 1973). In stoichiometric HAP and ClAp, the FAP mirror plane becomes a glide plane because of ordering in the b direction.

The transition from monoclinic to hexagonal occurs at 211.5 °C (van Rees et al., 1973) for HAP, and at about 200 °C for ClAp (Prener, 1967). This is a fairly simple displacive transition. The transition is probably second order, a conclusion allowed by analysis of the existing heat-capacity data for HAP (Egan et al., 1950, 1951a) and supported by the structural refinements of Schaeken et al. (1975).

The site for the X ions lies on the sixfold screw axis. In FAP, the F ion is situated on the mirror plane in the middle of a triangle of Ca ions. The hydroxyl ion is displaced slightly above or below the plane of the Ca triangle, and the Cl ion is displaced further still (Sudarsanan and Young, 1978), destroying the mirror symmetry. Ordering of the displacement direction, i.e., regular alternation of the OH or Cl ion above or below the plane produces a glide plane in place of the mirror and changes the symmetry axis from 6₃ to 2₁. The size and alternating displacement of the X ions are reflected in the unit-cell dimensions of the end-members (Sudarsanan and Young, 1978; see Table 1, this paper). The dimensions given by Sudarsanan and Young (1978) are for "hexagonal" end-members; the monoclinic b axis is equal to twice the hexagonal a axis, and the monoclinic unit cell is double the size of the hexagonal one.

It is difficult to synthesize stoichiometric HAP and ClAp because of the necessary ordering. Vacancies in the OH or Cl position will act to stabilize the mineral in its hexagonal form (Prener, 1971). Low-temperature syntheses of HAP have been clearly demonstrated to be nonstoichiometric with regard to hydroxyl content (Meyer, 1979; Posner et al., 1984; Arends et al., 1987) and may also

contain carbonate. An extensive search of the literature failed to produce any reports of monoclinic HAp produced by low-temperature precipitation. Hence precipitation experiments provide a useful analogue for human dental material and for phosphorite deposits, but are not as useful for high-temperature igneous problems or for characterization of stoichiometric end-members. The crystalline structure of HAp is very sensitive to the temperature and method of synthesis (Skinner, 1968, 1973, 1974; Wier et al., 1972; Arends et al., 1987). It will also dehydrate at high temperatures, with a dehydration peak at 705 °C in vacuum for hydrothermally grown HAp (Skinner et al., 1975) and slightly higher in air for low-temperature HAp precipitates (Arends et al., 1987). Comparison of the standard-state data derived by Duff (1971a, 1971b) for the Gibbs free energy of HAp and FAp with that derived by other means (Egan et al., 1950, 1951b; Gottschal, 1958; Farr and Elmore, 1962; Smirnova et al., 1962; Jacques, 1963; Valyashko et al., 1968; Westrich and Navrotsky, 1981; see Table 1) shows that Duff's data are anomalously more positive, unless a measurement error of $\pm 30 \text{ kJ} \cdot \text{mol}^{-1}$ is considered. No reliable data exist for ClAp, probably because of similar difficulties in synthesis and its instability at high temperature (Prener, 1967, 1971). Still more problems occur in low-temperature studies of FAp-HAp precipitation. The high-energy surfaces of the fine precipitates become essentially coated with F ions, so that the "equilibrium" values of F concentration in the aqueous phase reflect a state more akin to saturation with fluorapatite than saturation with a fluoro-hydroxyapatite (Wier et al., 1972; Driessens, 1979).

It has been demonstrated that apatites grown hydrothermally give better results with regard to stoichiometry for HAp (Perloff and Posner, 1956; Mengeot et al., 1973; Eysel and Roy, 1973) and ClAp (Roufosse et al., 1973; Ruzsala and Kostiner, 1975). Flux-grown apatites also give good results (Prener, 1967, 1971; Eysel and Roy, 1973; Roy et al., 1978). Thermodynamic data determined on apatites prepared by high-temperature syntheses are therefore more likely to yield reliable results than those deduced from apatites synthesized at low temperature.

Mixing behavior at the atomic scale

The fundamental problem in examination of a solid solution may be viewed as identification of the differences between the end-members and the mixed form. These differences can be examined as differences in crystal structure and atomic interaction, which would be quantified on the macroscopic scale as nonideal thermodynamic functions of mixing. For the apatite solid solutions at geologic temperatures ($> 200 \text{ }^\circ\text{C}$), where apatites are hexagonal, this problem could be stated as identification of the forms of interaction between halogens and the hydroxide radical.

Results of several avenues of inquiry have demonstrated that the halogens interact with the hydroxide ion on

adjacent sites at 25 °C. Structural refinements of X-ray diffraction data show that the halogens are pulled slightly off the position occupied in pure end-members (Sudarsanan and Young, 1978) toward neighboring hydroxide groups. The interaction implied by these refinements is supported by spectroscopic data. An unusual result of IR spectroscopic studies is that hydroxide interaction with chloride is more pronounced than that of fluoride (Dykes and Elliott, 1971; Maiti and Freund, 1981). Arguments based on electronegativities would suggest that hydrogen bonding would be greater between an hydroxide and a fluoride, whereas the reverse is found, principally because of the large size of chloride ion. The existence of the hydrogen bonding would lead to negative excess free energies of mixing (Maiti and Freund, 1981). However, the lattice strain associated with incorporating a large chloride ion into a hydroxyapatite would possibly contribute to positive deviations (Dykes and Elliott, 1971; Maiti and Freund, 1981), owing to the proximity of the adjacent oxygens and calciums. Low-temperature studies (Duff, 1972) show negative deviations from ideal solution along the join ClAp-HAp. This information is of uncertain importance without information on the structural state of the precipitates, given the role of vacancies in stabilization of hexagonal ClAp and HAp (Prener, 1967, 1971; Mackie et al., 1972).

Existing FAp-HAp data show that complete solid solution of the two end-members is possible (Freund and Knobel, 1977). Some unfavorable energetic effects may be present at low HAp contents in FAp, because of the interaction of a fluoride with the oxygen ion of an adjacent hydroxide dipole (Freund and Knobel, 1977). The behavior expected of FAp-HAp solid solutions would be negative deviations from ideality across the entire range of compositions at temperatures of 25 °C and higher (Schacken et al., 1975). These negative deviations from ideality are confirmed by Duff (1971b), but again, the role of vacancies in these low-temperature studies is uncertain.

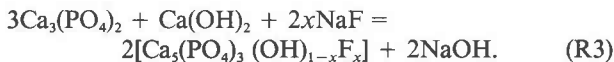
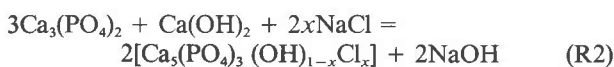
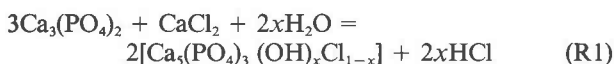
DATA BASE

The apatite solid solution may be thought of as three binaries: FAp-ClAp, FAp-HAp, and ClAp-HAp. Data for the FAp-ClAp join are limited to studies by Nacken (1912) and Prener (1967). Neither study is suitable for rigorous analysis. The FAp-HAp join has been studied at magmatic temperatures and pressures by Biggar (1967), Latil and Maury (1977), and Korzhinskiy (1981). Published studies of ClAp-HAp include those by Ekstrom (1973), Ruzsala and Kostiner (1975), Latil and Maury (1977), and Korzhinskiy (1981).

Latil and Maury (1977) presented the first comprehensive characterization of apatites of binary and ternary (FAp-HAp-ClAp) composition under magmatic or hydrothermal conditions. Experiments were conducted at 300–600 °C and 200 and 1000 bars. The results of this study clearly demonstrated that apatite stabilities are $\text{FAp} > \text{HAp} > \text{ClAp}$. Further, chlorapatites will partially re-

equilibrate with a F-bearing fluid, at 600 °C and 1 kbar, although this reaction does not proceed to completion within 3 weeks. FAp will not re-equilibrate with water or a Cl-bearing fluid at the same conditions, in agreement with the results of Ekstrom (1973). Re-equilibration of HAp is intermediate between the two: it will partially re-equilibrate with a F-bearing fluid, but not a Cl-bearing one.

Mathematical analysis of the results of Latil and Maury (1977) is not straightforward because complete data are lacking. These authors measured F and Cl in apatites and hydrothermal fluid after quench, but these values alone are not enough to fully determine the system in the presence of other components. Apatites were synthesized by the reactions



The Na component of the fluid in Reactions 2 and 3 is the most problematic because Na is readily accepted by the apatite structure (Young and Munson, 1966; E. J. Young et al., 1969; Ito, 1968; Cockbain, 1968; Hagen, 1973; Featherstone et al., 1983). As a first approximation, the reported total chloride or fluoride was recast as HCl or HF. We readily acknowledge that this may be incorrect, because

$$m_{\text{Cl total}} = m_{\text{HCl}} + 2m_{\text{CaCl}_2} (\pm m_{\text{NaCl}})$$

for the fluid phase, where m is molality. The effects of introduction of a Na component can be examined only for the 500 °C experiments.

The use of a sodium halide as a source for the halogen introduces a twofold problem. First, the aqueous and crystalline phases cannot be fully described without measurement of Na in at least one phase, accompanied by mass-balance calculations. Second, the introduction of Na into the apatite structure produces a charge deficiency that is likely to be balanced by the formation of a vacancy in the place of OH. The problem of the Na component could not be successfully resolved to our satisfaction, because Na partitioning between apatite and fluid is apparently more complex than can be accounted for with several different simple assumptions for calculating HAp contents. In the end, these data were not included in the determination of standard-state data.

The data of Korzhinskiy were more rigorously derived than earlier studies. The fugacity of HCl was buffered in these experiments by Ag-AgCl and solid-state external H_2 buffers after the double-capsule methods of Frantz and Eugster (1973), Chou and Frantz (1977), and Chou (1987).

Experimental methods in this study were essentially sound. However, in the experiments at 1 and 2 kbar,

pressure was not measured during the course of the experiment, but calculated from the P - V - T relations of the aqueous pressure medium. Error in these pressures is stated as 10% (Korzhinskiy, 1981).

We have accepted all of Korzhinskiy's data except those obtained using the CuO-Cu₂O buffer. In these experiments, the chloride content of the fluid was calculated rather than measured. In all experiments that were modeled, the CuO-Cu₂O compared poorly with other results.

The data of Ruzala and Kostiner (1975) were included because a chance existed that the results were near equilibrium. Their study was designed to grow large crystals along the join ClAp-HAp, and a temperature gradient of 20 °C was imposed on the 8-cm Au capsules. The growth zone of the crystals was 425 °C at a pressure of 3.57 kbar. It is difficult to determine the effects of the thermal disequilibrium on the results, but in the final analysis there is fair agreement among the data determined in this study and those of Korzhinskiy (1981). One data point was rejected from these experiments, that at the highest concentration of HCl. The results of this run are the same as one at lower HCl concentrations, suggesting that perhaps the capsule material was being dissolved, lowering the concentration of HCl in the fluid. Standard-state data determined with or without this point are essentially identical, although the sign of W_G changes.

The data set for the FAp-HAp models is acquired from the same sources as the ClAp-HAp data. Latil and Maury's data set is more extensive in its investigation of temperature effects, but the experimental products were synthesized by Reaction 3 given above, and the introduction of the Na component again raises questions that could not be successfully resolved. The data of Korzhinskiy were obtained using a Ca(OH)₂-CaF₂ buffer. External H_2 buffers were not used.

For the purposes of this study, the thermodynamic data of Robie et al. (1979) were adopted. The heat capacities, standard-state enthalpies, and entropies of all the reactants were used as published except for the enthalpy of FAp and the molar volumes of the apatite end-members. For the enthalpy of FAp we used the more recent data of Westrich and Navrotsky (1981). The molar volumes of the end-member apatites were taken from Sudarsanan and Young (1978). Changes in a and c axes for the apatite binaries have been repeatedly shown to be linear with respect to composition (FAp-ClAp: Wallaey, 1952; Sudarsanan and Young, 1978; HAp-FAp: Schaecken et al., 1975; HAp-ClAp: Ekstrom, 1973; Ruzala and Kostiner, 1975; Maiti and Freund, 1981). Fugacities of H_2O were taken from Burnham et al. (1969).

As a result of the difficulties in HAp syntheses discussed above, special attention was paid to the HAp standard-state data. Robie et al. (1979) cited Egan et al. (1950) as the source of the thermodynamic data for HAp. Careful reading indicates that the HAp was monoclinic although Egan et al. (1950) were unaware of the fact. The X-ray diffraction peaks indicative of monoclinic symmetry were evidently first registered in the ASTM files

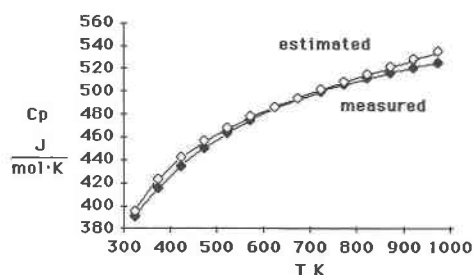


Fig. 1. Comparison of measured values of the heat capacity of FAp with those calculated by methods discussed in the text. Open diamonds are calculated values.

(Egan et al., 1950) for ClAp. The significance of these peaks was not recognized until some time later for HAp (Elliott, 1971; Elliott et al., 1973). Egan et al. (1950) noted the presence of these peaks in the diffraction patterns of their HAp. They were puzzled by the apparent contamination of their HAp with Cl, when none had been used in the synthesis. With the benefit of hindsight, we interpret these peaks to indicate monoclinic HAp rather than a contaminated sample.

Heat capacity of ClAp

Rather than solve for $\Delta G_{T,P}^0$ for ClAp (e.g., Spencer and Lindsley, 1981), a heat capacity (C_p) function was estimated for ClAp. In the absence of measurements, an empirical value may be calculated by fairly simple (Helgeson et al., 1978) or more sophisticated techniques (Robinson and Haas, 1983; Berman and Brown, 1985). The data base required for the latter two methods does not exist for phosphates, so a small modification of the additive method of Helgeson et al. (1978) was adopted. The measured heat capacity (Robie et al., 1979) of FAp and HAp was compared to a value calculated as

$$C_{p,HAp} - \frac{1}{2}C_{p,Ca(OH)_2} + \frac{1}{2}C_{p,CaF_2} = C_{p,FAp} \quad (1)$$

$$\text{and } C_{p,FAp} - \frac{1}{2}C_{p,CaF_2} + \frac{1}{2}C_{p,Ca(OH)_2} = C_{p,HAp} \quad (2)$$

$$\text{or } C_{p,FAp} - \frac{1}{2}C_{p,CaF_2} + \frac{1}{2}C_{p,CaCl_2} = C_{p,ClAp} \quad (3)$$

Heat capacities on the left-hand side are measured; those on the right, calculated. Heat capacities of the calcium hydroxide and calcium halides are also from Robie et al. (1979).

Good agreement is found between the calculated and the measured values for HAp and FAp (Figs. 1 and 2); the divergence of the two methods at lower temperature is probably due to the changes in HAp heat capacity at the monoclinic-hexagonal transition. The higher-temperature divergence of calculated and measured values of the heat capacities is due to the questionable extrapolation of the heat-capacity function for $Ca(OH)_2$: above 580 °C, $Ca(OH)_2$ is unstable with respect to CaO.

The C_p function for ClAp used in the modeling was calculated from that of FAp. This avoids the uncertainties introduced by the use of $Ca(OH)_2$. As discussed above,

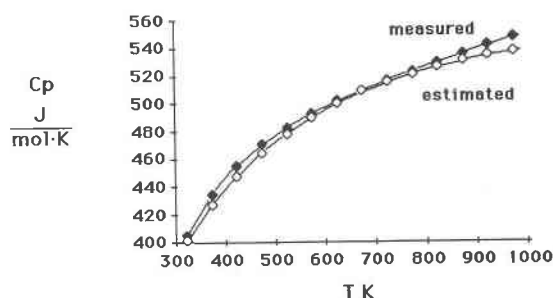


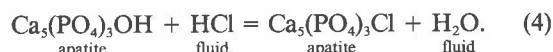
Fig. 2. Comparison of measured values of the heat capacity of HAp with those calculated by methods discussed in the text. Open diamonds are calculated values.

synthesis of FAp is easier than that of HAp, and the thermodynamic data are more reliable. The estimated heat-capacity function for ClAp is $C_p = 805.099 - (5.9302 \times 10^{-2})T + (5.3032 \times 10^5)T^{-2} - (7.1358 \times 10^3)T^{-0.5} + (3.3245 \times 10^{-6})T^2 - (6.4235 \times 10^7)T^{-3}$, in $J \cdot mol^{-1}$.

The use of a heat capacity calculated from FAp in the model yields thermodynamic data that are identical, within error, with values derived using the C_p function derived from HAp. In the temperature regimes of the experiments, the two give nearly identical results for heat capacity. However, we believe that the data derived from FAp may be extrapolated to higher temperatures with greater confidence than if a calculated C_p that relied on the $Ca(OH)_2$ heat capacity were used.

METHODS

Reactions 1 to 3 are usually written as exchange equilibria such as



The Gibbs free energy at the temperature and pressure of interest for Equilibrium 4 can be expressed as

$$\Delta G_{T,P} = \Delta H^0 - T\Delta S^0 + \int \Delta C_p dT - T \int (\Delta C_p/T) dT + \int \Delta \bar{V} dP, \quad (5)$$

where T is temperature (in kelvins), P is pressure, $\Delta G_{T,P}$ is the change in Gibbs free energy of the reaction at temperature and pressure, ΔH^0 is the change in standard-state enthalpy for the reaction, and ΔS^0 is the change in standard-state entropy for this reaction. The standard state is the pure substance at 298.15 K and 1 bar. $\Delta \bar{V}$ is the change in molar volume for the reaction, and ΔC_p is the change in heat capacity of the reaction.

For Equilibrium 4, the equilibrium constant is

$$K = (a_{ClAp}^{\Delta P} f_{H_2O}^{\text{fluid}}) / (a_{HAp}^{\Delta P} f_{HCl}^{\text{fluid}}). \quad (6)$$

The symbol a_j^i denotes activity of the j th component in the i th phase, and f_j^i is the fugacity of the j th component in the i th phase. The activity of the apatite components may be written as

$$a_{HAp}^{\Delta P} = X_{HAp}^{\Delta P} \gamma_{HAp}^{\Delta P}, \quad (7)$$

TABLE 2. Results of solution models

Reference	T (°C)	P (kbar)	W_G (kJ/mol)	Standard error (±)	$\Delta^{\circ}G^{\circ}$ (kJ/mol)	Standard error (±)	r^2
Regular solution model							
Latil and Maury (1977), Reaction 2	300	0.216	-17.625	3.149	-6774.729	0.389	0.94
Ruszala and Kostiner (1975)	425	3.571	-0.386	5.682	-6855.091	3.671	0.002
Latil and Maury (1977), Reaction 2	500	1	-14.959	7.698	-6872.725	0.838	0.791
Latil and Maury (1977), Reaction 1	500	1	8.327	2.357	-6900.671	2.916	0.862
Latil and Maury (1977), Reaction 2	600	1	-20.549	35.901	-6917.508	3.841	0.098
Korzhinskiy (1981)	500	1	-3.837	1.544	-6899.942	1.658	0.507
Korzhinskiy (1981)	600	1	-0.253	2.437	-6945.956	3.335	0.001
Korzhinskiy (1981)	600	2	-0.518	0.67	-6951.066	1.106	0.062
Korzhinskiy (1981)	700	1	0.983	2.143	-6988.663	2.914	0.029
Korzhinskiy (1981)	700	2	-0.204	1.686	-6995.464	2.776	0.001
Korzhinskiy (1981)	700	4	-0.307	2.96	-7003.468	2.815	0.005

Reference	T (°C)	P (kbar)	$W_{cl,h}$ (kJ/mol)	Standard error (±)	$W_{h,cl}$ (kJ/mol)	Standard error (±)	$\Delta^{\circ}G^{\circ}$ (kJ/mol)	Standard error (±)	r^2
Latil and Maury (1977), Reaction 2	300	0.216	74.503	47.06	183.196	138.319	-6710.589	0.364	0.974
Ruszala and Kostiner (1975)	425	3.571	46.797	54.562	-26.013	36.383	-6878.207	3.859	0.27
Latil and Maury (1977), Reaction 1	500	1	-25.945	4.327	-9.428	26.632	-6906.18	3.906	0.922
Latil and Maury (1977), Reaction 2	600	1	329.294	2158.087	824.684	5626.865	-6589.891	4.681	0.107
Korzhinskiy (1981)	500	1	-11.067	13.184	4.87	8.301	-6899.419	1.642	0.597
Korzhinskiy (1981)	600	1	-19.797	34.327	-39.426	56.903	-6950.842	3.427	0.077
Korzhinskiy (1981)	600	2	-0.942	4.14	7.277	5.002	-6954.568	2.065	0.191
Korzhinskiy (1981)	700	1	18.275	7.839	-0.849	5.505	-6999.988	2.194	0.528
Korzhinskiy (1981)	700	2	-6.435	4.56	4.221	5.938	-7000.847	2.575	0.227
Korzhinskiy (1981)	700	4	6.636	48.004	4.365	28.096	-7008.676	3.944	0.024

where X is mole fraction and γ is the activity coefficient. Hence the equilibrium constant may be rewritten as

$$K = [(X_{ClAp}^{Ap} f_{H_2O}^{fluid}) / (X_{HAp}^{Ap} f_{HCl}^{fluid})] (\gamma_{ClAp}^{Ap} / \gamma_{HAp}^{Ap}). \quad (8)$$

The activity coefficients for the apatite components are the item of interest in this case. Noting that $\Delta G_{T,P} = -RT \ln K$, we may separate out the activity coefficients and write

$$\Delta G_{T,P} + RT \ln [(X_{ClAp}^{Ap} f_{H_2O}^{fluid}) / (X_{HAp}^{Ap} f_{HCl}^{fluid})] = -RT \ln (\gamma_{ClAp}^{Ap} / \gamma_{HAp}^{Ap}). \quad (9)$$

The second term on the left hand side of Equation 9 is now not an equilibrium constant, K , but would be better written as K' , the apparent equilibrium constant. It is represented as such in Figures 3 and 5.

There are several methods for modeling the activity coefficients. The assumption of ideality implies that the activity coefficients are equal to unity. The solid solution may be described as symmetrical or asymmetrical (Thompson, 1967; Navrotsky, 1987). In the case of an asymmetrical solid solution, the activity coefficient of a phase component of apatite may be written in terms of binary Gibbs free-energy interaction parameters such that

$$RT \ln \gamma_{ClAp} = X_{HAp}^2 \{ (W_G)_{Cl,H} + 2[(W_G)_{H,Cl} - (W_G)_{Cl,H}] X_{ClAp} \}$$

or

$$RT \ln \gamma_{HAp} = (W_G)_{H,Cl} (2X_{ClAp}) + (W_G)_{Cl,H} (X_{HAp}^2 - 2X_{ClAp}). \quad (10)$$

$(W_G)_{Cl,H}$ is the Gibbs free-energy interaction parameter of ClAp, and $(W_G)_{H,Cl}$ that of HAp. In the case of a regular solution, $(W_G)_{Cl,H} = (W_G)_{H,Cl}$, the equations may be sim-

plified. None of these models may be selected a priori, so both the symmetrical solution and asymmetrical solution models were tested.

No reliable thermodynamic standard-state data exist for ClAp, so the experimental data were reduced in such a way as to yield standard-state data for ClAp. Defining, for convenience, $\Delta G_{T,P}^* = \Delta G_{T,P} - (\Delta H_{ClAp}^0 - TS_{ClAp}^0)$, and $(\Delta H_{ClAp}^0 - TS_{ClAp}^0) = \Delta^{\circ}G^{\circ}_{ClAp}$, Equation 9 can be rewritten as

$$\Delta G_{T,P}^* + RT \ln K' = -\Delta^{\circ}G^{\circ}_{ClAp} + (W_G)_{H,Cl} (2X_{ClAp} + X_{ClAp}^2 - 2X_{HAp}) - (W_G)_{Cl,H} (X_{HAp}^2 + X_{ClAp} + 2X_{HAp}). \quad (11)$$

Equation 11 was expressed with two (or three, in the case of an asymmetric solution) known parameters: (1) ΔG^* plus the apparent equilibrium constant term and (2) the coefficient(s) for the W_G term(s). These equations were solved by least-squares regressions, yielding the $-\Delta^{\circ}G^{\circ}_{ClAp}$ of chlorapatite and the W_G parameter(s). Regression of $\Delta^{\circ}G^{\circ}$ with respect to temperature gives ΔH^0 and S^0 for ClAp.

RESULTS

ClAp-HAp models

The symmetric solution and asymmetric solution models produced roughly similar results for the $\Delta^{\circ}G^{\circ}_{ClAp}$. These results are in Table 2. Graphical presentation of the symmetric solution model is in Figures 3a to 3k. In general, the symmetric solution model gave small (<20 kJ·mol⁻¹) negative deviations (Table 2). There appears to be no regular temperature dependence of W_G above

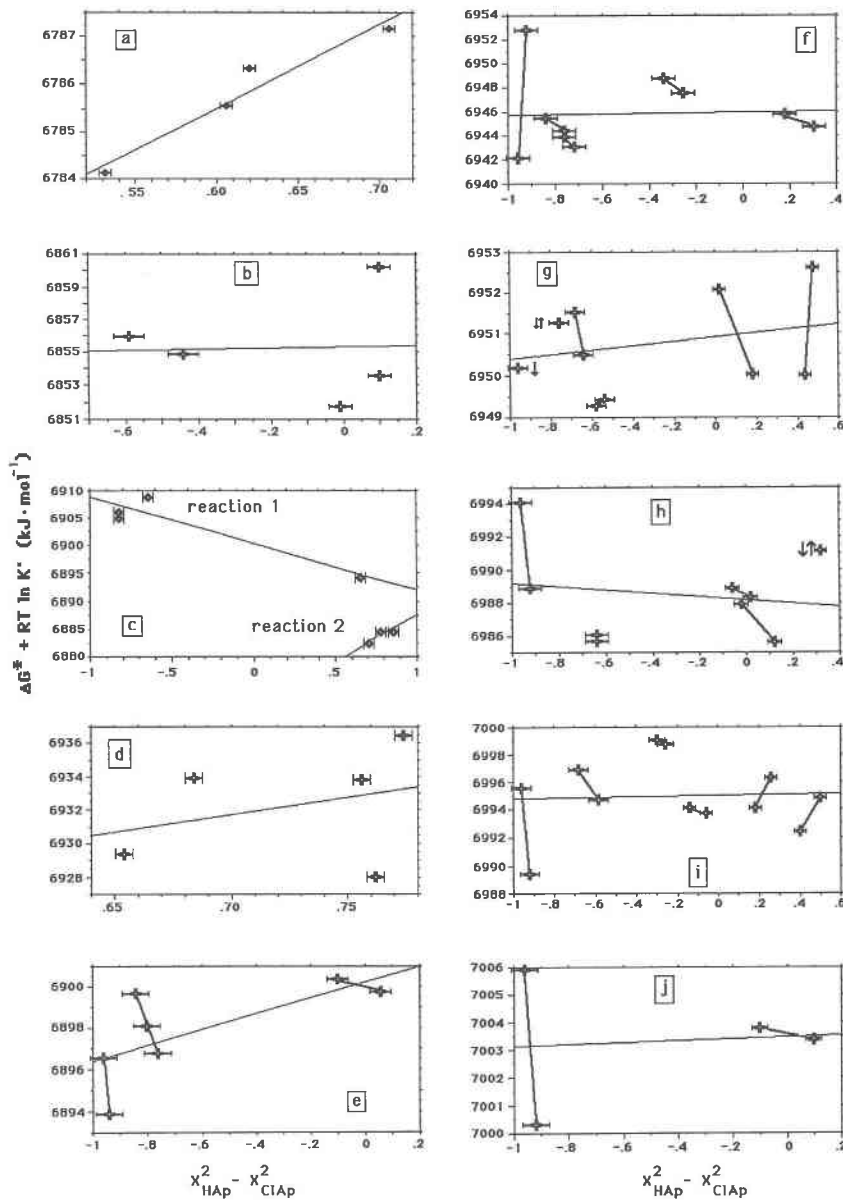


Fig. 3. Graphical presentation of results of the symmetrical solution model. On these diagrams, the slope is equal to the negative W and the intercept equals negative $\Delta^{\circ}G$ as discussed in the text. Lines connect reversed runs. A double arrow indicates a mixture of HAp and ClAp as the starting material, a single arrow indicates the direction of the reversal. Vertical uncertainties generally exceed the size of the graph. Note that the points were automatically spaced so as to fill the page, resulting in some large interpoint spaces that are an artifact of plotting rather than poor agreement. (a) Latil and Maury (1977) data,

300 °C and 216 bars. (b) Ruszala and Kostiner (1975) data, 425 °C and 3.57 kbar. (c) Latil and Maury (1977) data, 500 °C and 1 kbar. Reaction 1 is a Na-free experiment. Reaction 2 is Na-bearing. All other Latil and Maury experiments used Reaction 2. (d) Latil and Maury (1977) data, 600 °C and 1 kbar. (e) Korzhinskiy (1981) data, 500 °C and 1 kbar. (f) Korzhinskiy (1981) data, 600 °C and 1 kbar. (g) Korzhinskiy (1981) data, 600 °C and 2 kbar. (h) Korzhinskiy (1981) data, 700 °C and 1 kbar. (i) Korzhinskiy (1981) data, 700 °C and 2 kbar. (j) Korzhinskiy (1981) data, 700 °C and 4 kbar.

500 °C. W_c is equal to 0 within error. The apparent existence of the deviations from ideal solution is probably a result of the scatter of the data rather than a consequence of nonideal behavior. Above 500 °C, the ClAp-HAp solid solution may be treated as ideal. It is impor-

tant to note that in some of the sets of experiments, the entire compositional range of the solid solution is not covered. Where the results are more complete, the conclusion of near-ideality is consistent with experimental error.

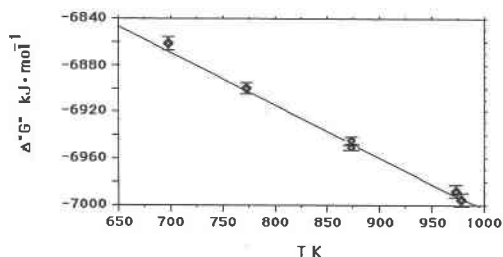


Fig. 4. Regression of the Korzinskiy (1981) data. Slope is negative entropy, intercept is enthalpy of formation from the elements. Results of 425 °C experiments are shown for comparison. Results of the 425 °C and 700 °C, experiments at 4 kbar are not included in the regression. Errors are 2σ .

An interesting result was obtained from the data of Latil and Maury (1977) for Reaction 1. These data are in good agreement at 500 °C and 1 kbar with the results of Korzinskiy (1981; Fig. 4 of this paper), although very different W_G values were derived. The agreement is not as good (+10 kJ/mol) for the Reaction 2 results at the same conditions. The Na evidently is not completely accounted for, suggesting that the Na partitions to some degree between fluid and apatite rather than being totally consumed in the formation of apatite. There is insufficient information to perform a mass-balance calculation. The different results derived from Reaction 2 as compared to Reaction 1 and to Korzinskiy's data cast some doubt on the results of the 300 °C experiments, which were performed with Reaction 2.

Analysis of the errors involved in these calculations is difficult. The problem is magnified by the poor fit of the model regressions to the data. The error in apatite compositions is ± 1 mol% (Latil and Maury, 1977) and ± 2 mol% (Ruszala and Kostiner, 1975; Korzinskiy, 1981). Propagation of uncertainties gives rise to an uncertainty of as much as ± 15 kJ·mol⁻¹ in $\Delta^{\circ}G^{\circ}_{\text{ClAp}}$ intercepts of the regressions. This uncertainty generally exceeds the vertical dimension of Figures 3 and 5. Of this uncertainty, ± 8 kJ·mol⁻¹ results from the use of the data of Robie et al. (1979), for which error is quoted as ± 5 kJ·mol⁻¹. However, the standard error of the $\Delta^{\circ}G^{\circ}_{\text{ClAp}}$ at each temperature and pressure calculated from regression statistics is about ± 5 kJ·mol⁻¹. This is the standard error quoted in Table 2.

The values for $\Delta^{\circ}G^{\circ}_{\text{ClAp}}$ may be regressed to give estimates of ΔH° and S° at 298 K and 1 bar for ClAp. An assumption required for this regression is that corrections for pressure are accounted for by $\int \Delta \bar{V} dP$. This may not be strictly true, for differences of about 3.5 kJ·mol⁻¹ per kilobar exist between $\Delta^{\circ}G^{\circ}_{\text{ClAp}}$ for the 1-, 2-, and 4-kbar regressions of Korzinskiy's data. This may reflect non-ideal volumes of mixing, but it is more likely that these discrepancies arise from variations in thermodynamic behavior in the components of the fluid phase as a function of pressure. We prefer the latter explanation, in view

of the recognized simplicity of apatite volumes of mixing and the known complexities of supercritical fluid phases (Eugster and Baumgartner, 1987; Holloway, 1987; Sverjensky, 1987). For this reason, and because of the very limited size, the 4-kbar data of Korzinskiy (1981) are not included in the regression.

Two sets of standard state data can be obtained. The best estimate would probably utilize only Korzinskiy's data: $\Delta H^{\circ}_{\text{ClAp}} = -6548.027$ kJ·mol⁻¹, and $S^{\circ}_{\text{ClAp}} = 457$ J·mol⁻¹·K⁻¹, which has r^2 equal to 0.993 (Fig. 3). This could more comfortably cover the range of temperatures found in natural magmatic systems and could be extrapolated to higher temperatures with greater confidence. Inclusion of the data at 425 °C yields a $\Delta H^{\circ} = -6517.891$ kJ·mol⁻¹, and $S^{\circ} = 490$ J·mol⁻¹·K⁻¹. This covers a larger range of temperatures, but is less reliable because of the uncertainties associated with temperature gradients in the 425 °C experimental charges. In addition, it is uncertain if the conditions of ideal solution may be extended to lower temperature.

These standard-state data are more positive than the values determined by Valyashko et al. (1968) or the values re-calculated from Duff's (1972) data by Vieillard and Tardy (1984) (see Table 1). The close agreement between our value and that of Duff (1972) is probably fortuitous. The values determined for ΔH° by Gottschal (1958) (quoted by Valyashko et al., 1968) and the value estimated for entropy (Valyashko et al., 1968) also compare poorly to those given here. This may result from the presence of nonstoichiometric ClAp in the earlier studies, as discussed above. However, our data do not explicitly account for the monoclinic-hexagonal transition of ClAp. Thus our standard-state data, projected from high temperature, represent a hypothetical "hexagonal" ClAp at 298.15 K.

FAP-HAP models

Attempts were made to fit the data with symmetric and asymmetric models for FAP-HAP solutions. The data of Latil and Maury (1977) were reduced as discussed above. Korzinskiy's experiments were treated differently. On the assumption that the Ca(OH)₂-CaF₂ "buffer" was effective, the reaction was rewritten as a solid-solid exchange reaction between "buffer" and apatite, rather than as a fluid-apatite exchange.

Unfortunately there are insufficient data to reliably fit the data by least-squares regression. Korzinskiy performed experiments starting from end-member compositions. Therefore there are only two data points, or one reversed point per regression, per experiment at each pressure, as illustrated in Figures 5a to 5c, that constrain the mixing model. To a first approximation, the effects of pressure on FAP-HAP mixing may be neglected, because of the close similarity in their unit-cell dimensions, and the data may be grouped by temperature.

It is immediately apparent that the experiments that started with FAP are not in good agreement with those that started with HAP. If least-squares regression is performed on these poorly reversed points, the resulting line

simply connects the group of points that were synthesized from FAp with the group resulting from HAp starting material. The correct line should not connect these points, but should pass between them at some unknown angle to the connecting line. The slope of the connecting line and the compositional gap between reversals suggest that there is an immiscibility gap for FAp-HAp at these temperatures. Abundant evidence from other sources, however, suggests that the problem is not FAp-HAp immiscibility (Biggar, 1967; Duff, 1971b; Schaecken et al., 1975), but a failure of the FAp to re-equilibrate with the fluid (Ekstrom, 1973; Latil and Maury, 1977).

The data will allow an interpretation of ideal behavior: a line of zero slope can be drawn through the reversals. However, the intercept of such a regression will not equal zero. This implies that there are discrepancies in the standard-state data selected, but the validity of this implication requires further testing.

The data of Latil and Maury at 300, 400, and 500 °C indicate that a symmetric solution model is insufficient to describe the excess free energy of mixing. The excess Gibbs free-energy curves are less symmetric at higher values of X_{FAp} , which would correspond to higher concentrations of Na in the fluid, and probably in the experimental products. If the Na is accounted for by one of several simple assumptions, a symmetric solution model is sufficient to describe the data, but there are evidently discrepancies in the initial standard-state data, as in Korzhinskiy's results. The data are of insufficient quality to accurately determine the source of the discrepancies.

DISCUSSION

Ideal mixing in the case of the apatites implies that there is no significant interaction between the neighboring X ions. However, such interactions are known for the apatites at 25 °C: interactions may be detected by unit-cell refinements (Mackie and Young, 1974; Sudarsanan and Young, 1978), NMR (R. A. Young et al., 1969) and IR spectroscopy (Dykes and Elliott, 1971; Freund and Knobel, 1977; Maiti and Freund, 1981). However, at elevated temperatures, the expansion of the lattice is evidently sufficient to ease such interactions. This is supported by the observation of a shift in HAp and ClAp structures from monoclinic to hexagonal at about 200 °C. The data for ClAp-HAp solid solutions may be interpreted as representing near-ideal solution behavior between 500 and 700 °C. Because the Cl-OH interaction is greater than that of F and OH, we may also postulate that the FAp-HAp solid solution is likewise ideal. A major contributing factor to these interactions is size of the adjacent X ions; it is likely that ClAp-FAp solution is nearly ideal as well as these temperatures.

An interesting sidelight of the experimental data is that the reversals of Korzhinskiy (1981) and the re-equilibration experiments of Latil and Maury (1977) support earlier studies that concluded that apatite re-equilibration in nature is slower than that of biotite. Hydrothermal dissolution of FAp is apparently insignificant. In addition,

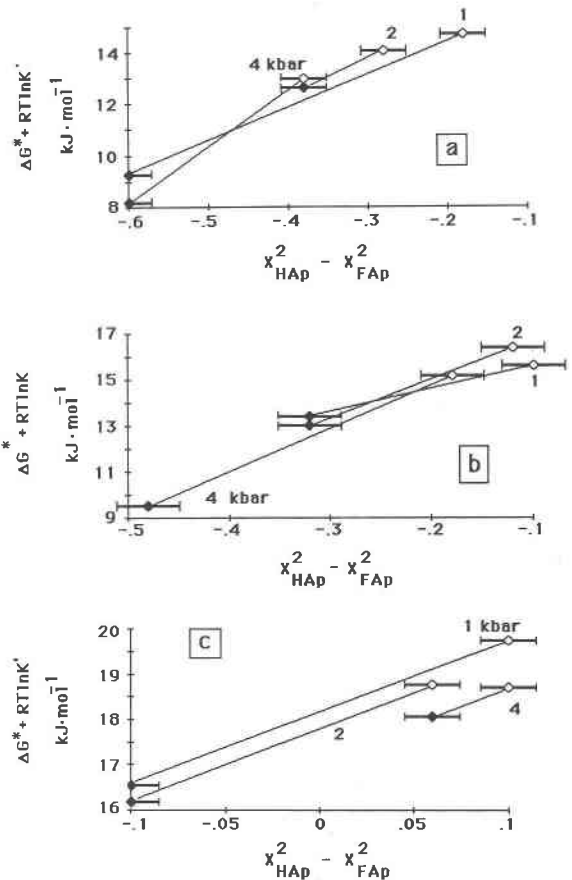


Fig. 5. Comparison of reversals of $\text{Ca}(\text{OH})_2\text{-CaF}_2$ experiments of Korzhinskiy (1981). Open diamonds are HAp starting materials, closed are FAp. Note that some FAp experiments have scarcely re-equilibrated. Numbers indicate pressure of run. (a) 500 °C; (b) 600 °C; (c) 700 °C. In this figure, slope equals W_G .

both HAp and ClAp exhibit retrograde solubility in water from ~300 to 600 °C and at 3 to 4 kbar (Mengeot et al., 1973; Roufousse et al., 1973). Experiments on the diffusivity of ^{18}O (Farver and Gilletti, 1988) showed that Durango FAp showed no signs of re-equilibration to HAp in experiments in H_2O to 1100 °C. In addition, diffusion of the Cl^- ion is apparently very slow. The linear column of X ion sites essentially limits diffusion to a direction parallel to the sixfold axis, because distances between adjacent columns are about three times greater than distances between X sites along this axis (Royce, 1974). Hence, activation energies between columns are much higher (Royce, 1974; Farver and Gilletti, 1988). Measured and modeled values of the energy of activation show that X-ion diffusion along the sixfold axis is most rapid for the F^- ions, less for the OH^- ion, and still less for O^{2-} (on the X site) (Tse et al., 1973). By implication, Cl^- diffusion is slower still (Tse et al., 1973). It should be noted that a relative immunity to re-equilibration by a diffusive mechanism does not imply an immunity to

wholesale dissolution and re-precipitation under appropriate conditions.

CONCLUSIONS

Thermodynamic analysis of previously published experimental data yields some insight into composition-activity behavior of apatite solid solutions. An additional benefit is a better understanding of the behavior of apatites under hydrothermal conditions. The data allow the following conclusions:

1. ClAp-HAp solid solutions may be considered to be essentially ideal at 500 °C and above.

2. FAp-HAp relationships are not clearly defined, but allow the interpretation of ideal solution behavior to be extended to the HAp-FAp solid solution at temperatures above 500 °C. This argument is supported by spectroscopic data.

3. Some uncertainty arises from the use of sodium halides in the experiments of Latil and Maury (1977), and in the effects of thermal disequilibrium on the results of the 425 °C experiments. This suggests that the results of the Korzhinskiy ClAp-HAp data set are preferable for use in understanding high-temperature geologic processes. However, fair agreement among the higher-temperature Korzhinskiy results and those of Ruszala and Kostiner at 425 °C suggests that our derived standard-state data may be used for lower-temperature problems with suitable caution. It is uncertain if the assumption of ideal behavior can be extended to these lower temperatures.

4. The experimental evidence supports the conclusions of earlier studies: apatite possesses a relative immunity to low-temperature re-equilibration by diffusive processes. High-temperature hydrothermal dissolution is also not significant in changing apatite compositions, especially FAp.

We are currently undertaking experiments to further clarify the mixing behavior of FAp-ClAp and HAp-FAp solid solutions.

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