

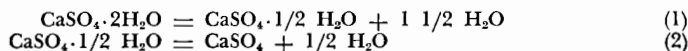
STABILITY RELATIONS IN THE SYSTEM $\text{CaSO}_4\text{-H}_2\text{O}$ AT HIGH TEMPERATURES AND PRESSURES*

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ABSTRACT. Phase equilibria in the system $\text{CaSO}_4\text{-H}_2\text{O}$ were investigated at water pressures up to 30 kb.

The following reactions have been studied:



Curve (2) intersects curve (1) at an invariant point located at approximately 85°C and 2 kb. Below this pressure calcium sulfate hemihydrate does not exist as a stable phase.

The location of the stability of bassanite in the P-T field suggests that bassanite is metastable in the reported natural occurrences.

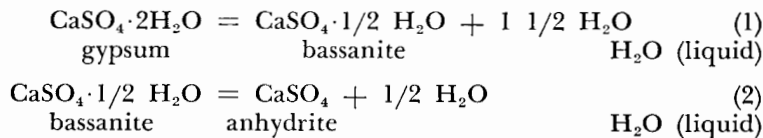
INTRODUCTION

The stability relations in the system $\text{CaSO}_4\text{-H}_2\text{O}$ are of geological interest because of the minerals gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4), and bassanite ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$). The former two are common in natural marine evaporite deposits. Bassanite is rare in nature but is the principal ingredient of plaster of Paris.

The binary system has been studied experimentally at 1 atm pressure by many investigators (for example, Partridge and White, 1929; Posnjak, 1938; Hill, 1937). Kelley, Southard, and Anderson (1941) obtained the thermochemical data on the solid phases of the system at 1 atm pressure. The equilibrium temperature for the gypsum-anhydrite transition was calculated to be at 40°C. MacDonald (1953) calculated the effect of pressure and H_2O activity on the reaction: gypsum = anhydrite + H_2O (liquid). There are no experimental data on the effect of high pressure on the transition.

Recently bassanite, calcium sulfate hemihydrate, has been reported from a number of natural environments, for instance Bundy (1956) reports its occurrence in Indiana salt beds. On the basis of experimental work and thermochemical data (MacDonald, 1953) bassanite is unstable relative to gypsum and anhydrite at 1 atm pressure at all temperatures. For these reasons the high-pressure phase relations in this system are of particular interest, and effort has been made to determine the stability field of calcium sulfate hemihydrate.

Equilibrium pressure-temperature curves have been determined for the following univariant reactions:



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EXPERIMENTAL METHOD

The starting materials used in the present investigation were Baker's analyzed reagent calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$), formed by heating the dihydrate at 100°C for a day, and anhydrite (CaSO_4) prepared by heating the dihydrate at 500°C for 4 days. Some experiments were carried out using natural gypsum and anhydrite. The gypsum was a large clear selenite plate from Kingman, Mohave County, Ariz., and the anhydrite was a large granular mass from New Cornelia Mine, Ajo, Pima County, Ariz. All starting materials were examined with the X-ray diffractometer. The experimental work was carried out in a piston-cylinder, high-pressure apparatus (Boyd and England, 1960). A chromel-alumel thermocouple junction was placed in contact with the gold sample capsule. Graphite tubing was used as an internal heating element. Temperature during the run was controlled manually by varying the power and was held within $\pm 5^\circ\text{C}$. All pressures were corrected for friction by approximately 8 percent and are probably correct to ± 1 kb. Starting materials were placed in sealed gold tubular capsules, 5 mm in length and 1 mm in diameter. Figure 1 shows the details of our experimental assembly.

In the course of an experiment, the pressure was first raised, with the furnace cold, to a pressure somewhat below the desired pressure. The temperature was then raised to the desired point over a period of approximately 10 minutes. The pressure was then increased to the desired value. The pressure and temperature were kept as constant as possible by manual control. At the end of a run the temperature of the sample was brought to room temperature in a few minutes by turning off the power to the furnace. The temperature drop is believed to be fast enough to prevent retrograde reaction in the system. Despite the large temperature gradient along the furnace, the gradient across the sample is believed to have been no more than a few degrees because of the small size of sample.

Equilibrium in the system was determined by sealing both pure, fine-grained reactants and mixtures of products and reactants with water in the gold tubes. The growth of one phase at the expense of another as indicated by major changes in X-ray diffractometer peak heights was used as a criterion in determining the stability fields. To our surprise, the direction of the reaction could normally be determined in times as short as 3 hours at temperatures of 100° and above.

PRIOR WORK

The only prior work on the reaction gypsum $\rightarrow$ bassanite and bassanite $\rightarrow$ anhydrite at high pressures is that published by Kennedy (1961). That work, however, was done in piston-anvil apparatus and was not considered to be reliable. Surprisingly, the reaction bassanite $\rightarrow$ anhydrite + water reported by Kennedy (1961) is essentially identical to the equilibrium boundary reported here. The reaction gypsum $\rightarrow$ bas-

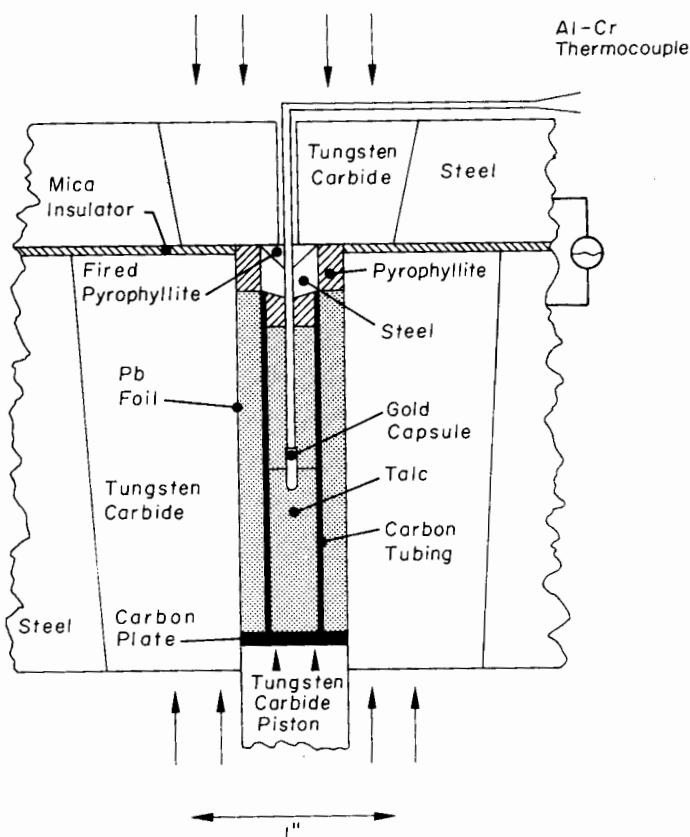


Fig. 1. Schematic drawing of the pressure cell.

sanite + water was reported to have a slight negative slope from work in anvil apparatus, but the results shown in this paper suggest a slight positive slope. The close agreement between piston-anvil results and hydrostatic results for both gypsum and calcite, both soft substances, contrasts markedly with the great disagreement between the two sets of data for various hard silicates (Kitahara and Kennedy, 1964).

EXPERIMENTAL RESULTS

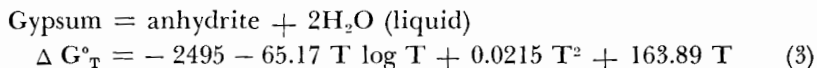
The experimental results from chemical reagent starting materials are listed in table 1. Figure 2 shows the equilibrium diagram for the reactions. Results from natural minerals, not plotted, lie about 5°C higher than those shown from very fine-grained chemical reagents. The difference is not significant and probably is due to the high surface energy of the artificial starting material. The products were identified by X-ray diffractometer. The hydration reactions were usually less complete, especially below 150°C, than the dehydration reactions. Both

curves are assumed to be equilibrium curves where water pressure is equal to the total pressure acting on the solid phases. Reaction curves for (1) and (2) show positive slope, but the slope for curve (2) is much steeper than that for (1). Therefore curve (2) intersects curve (1) at an invariant point located at about 85°C and 2 kb. Below this pressure the gypsum $\rightarrow$ anhydrite + water curve has been drawn to meet the recently determined 1 atm value of 58° for the gypsum-anhydrite equilibrium (Hardie, 1967).

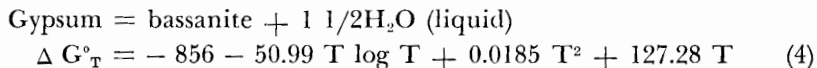
The "synthesis boundary" for the reactions gypsum $\rightarrow$ bassanite + water and for the reaction bassanite $\rightarrow$ anhydrite + water has been determined at 5 kb intervals to 30 kb. The boundary was reversed at most of these intervals, and the synthesis boundary is thus believed to be the equilibrium boundary. At low pressures the gypsum $\rightarrow$ bassanite + water boundary was not reversed but is a smooth extension of the equilibrium boundary determined at higher pressures.

THERMODYNAMIC CALCULATION

Kelley and others (1941) have obtained thermochemical data for the solid phase in the system $\text{CaSO}_4\text{-H}_2\text{O}$. They obtained for the reaction



This equation gives 313°K (40°C) as the temperature at which gypsum, anhydrite, and liquid water can coexist at 1 atm total pressure. This is reasonably consistent with the Hardie value of 58°C .



This equation gives 370°K (99°C) as the equilibrium 1 atm temperature. This value, 99°C , is in fair agreement with the value of 80°C obtained by extrapolating our experimental curve. MacDonald (1953) calculated the effect of pressure on the reaction in pure water. Since the ΔV (8.27cc) for the gypsum = anhydrite + $2\text{H}_2\text{O}$ (liquid) reaction is positive, an increase in total pressure will favor the formation of gypsum. Assuming ΔV is constant over the temperature interval 0°C to 50°C and the pressure interval 1 to 500 bars, MacDonald obtained the value of 85.4 bars/deg for the initial slope at 40°C . This is in remarkable agreement with 81 bars/deg obtained from the Hardie 1 atm value and our 500 bar value.

Recently Hardie (1967) has recalculated the equilibrium temperature using the available new thermochemical data and fixes the gypsum-anhydrite transition point at $46 \pm 22^\circ\text{C}$ in contrast to his experimental value of 58°C .

Zen (1965) calculated the intersection of curves (1) and (2) to be approximately 9 kb and 175°C , using methods analogous to those of MacDonald.

TABLE 1
Results of runs on $\text{CaSO}_4\text{-H}_2\text{O}$ system

Starting material	Temp, °C	Pres- sure, kb	Time, hours	Products
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	90	4	3	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	100	4	3	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaSO}_4 + 1/2\text{H}_2\text{O}$	110	4	4	CaSO_4
$\text{CaSO}_4 + 2\text{H}_2\text{O}$	90	5	3	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 + 2\text{H}_2\text{O}$	100	5	3	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	120	5	6	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaSO}_4 + 1/2\text{H}_2\text{O}$	130	5	3	CaSO_4
$\text{CaSO}_4 + 2\text{H}_2\text{O}$	110	10	3	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 + 2\text{H}_2\text{O}$	120	10	3	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 + 2\text{H}_2\text{O}$	160	10	3	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	160	10	6	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	170	10	3	CaSO_4
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	120	15	2.5	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	130	15	3	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	130	15	5.5	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	140	15	3	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 + \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	160	15	5	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 + \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	190	15	5	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	190	15	3	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	200	15	3	CaSO_4
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	210	15	2	CaSO_4
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	140	20	2.5	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	150	20	3	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	200	20	3	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	220	20	3	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	220	20	6	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	230	20	2	CaSO_4
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	250	20	3	CaSO_4
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	140	25	2	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	140	25	4	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	150	25	3	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	160	25	2.5	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	220	25	4	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	230	25	2	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	250	25	2	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	260	25	2	CaSO_4
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	160	30	1.5	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	160	30	4	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	170	30	2	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	200	30	2	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	260	30	2	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	260	30	6	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ grew
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	270	30	3	CaSO_4
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	290	30	2	CaSO_4
$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O} + \text{CaSO}_4$	320	30	3	CaSO_4

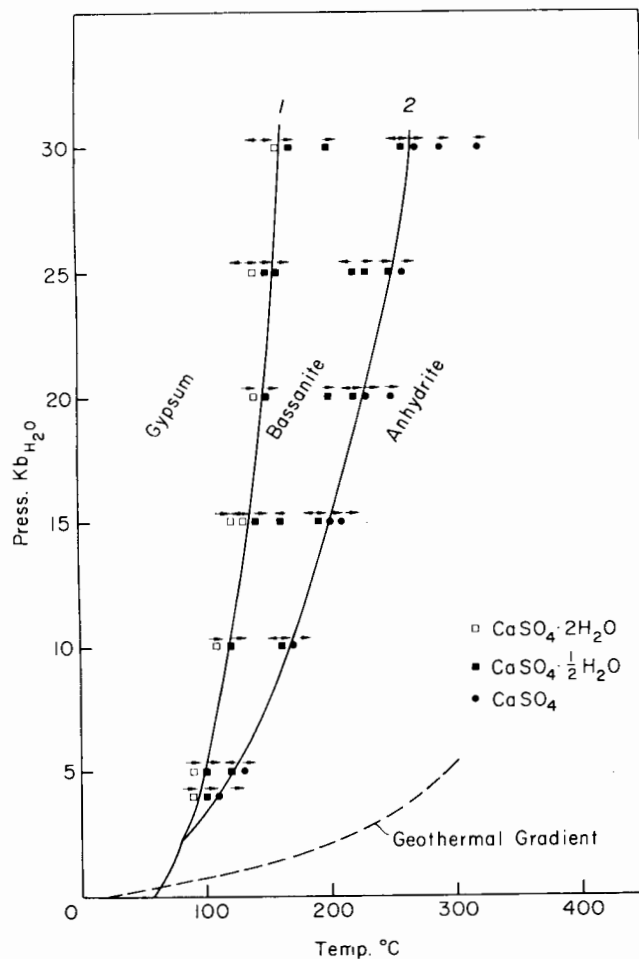


Fig. 2. Equilibrium diagram for the system $\text{CaSO}_4\text{--H}_2\text{O}$ (arrow shows direction from which equilibrium was approached).

We have attempted to intercompare our experimentally determined slopes with slopes for the various reactions computed from the thermodynamic data. In such calculations the assumption is normally made that the volumes of the solids at high pressure have essentially the same volumes as they have at 1 atm. This assumption is fairly good for silicates and is particularly useful where the volume change in reaction is large. However, in reactions involving bassanite, volume changes are extremely small, and depending on assumptions as to the compressibility of the various phases, even the sign of the slope of curve 1 is uncertain. Thus, the calculations become essentially meaningless when 1 atm data is used to compute the slopes at higher pressures and temperatures.

An additional problem exists with the uncertainty of the entropy of bassanite. Alpha soluble anhydrite has an entropy of approximately 26 e.u. whereas the hemihydrate, bassanite, has an entropy of approximately 32 e. u. X-ray patterns of the two phases are virtually identical. We have no certainty that our high-pressure product, which we call "bassanite", had a constant entropy or even a constant water content over the P-T range of 100° and 30 kb. Thus, an intercomparison between the measured slopes and calculated slopes is not warranted.

GEOLOGICAL CONSIDERATIONS

Gypsum and anhydrite are the most common of the sulfate minerals. There are many views as to whether both are primary precipitates or whether one is primary and the other is secondary. Pettijohn (1949) suggested that the original material of most gypsum beds was anhydrite. Bundy (1956) and Sund (1959) suggested that gypsum may be the only form of calcium sulfate precipitated from sea water. Stewart (1953) noted the possibility that either gypsum or anhydrite might occur as a primary precipitate. Recent experimental work at atmospheric pressure by Hardie (1967) showed that anhydrite is the stable phase at temperatures only above 58°C in pure water, but in NaCl saturated brines, anhydrite is stable above 18°C. This may be applicable at least to the genesis of some recent marine deposits. The relations of phases in older deposits have obviously been modified by the effect of post-depositional burial, and the present relationship between gypsum and anhydrite in most geological formations is secondary.

Bassanite occurs only rarely in nature. Palache, Berman, and Frondel (1951) state that bassanite is "Found in cavities of leucite-tephrite blocks thrown out during the April, 1906, eruption of Vesuvius. Also found with gibbsite in fumaroles of 1911". Bassanite has also been reported by Palmer (1959) as a mineral making up part of some fossil arthropods found in the Mohave Desert, and Bundy (1956) reported it as a very minor component of some gypsum-anhydrite deposits in southwestern Indiana. He believed it to be a metastable mineral in a transition zone between gypsum and anhydrite. It is clear from examination of our figure 2 that in all these circumstances, bassanite did not appear as a stable phase, and indeed it seems highly unlikely that bassanite can ever be a stable mineral within the Earth's crust. We concur with Zen (1965) who says "it appears that bassanite might be stable under high pressures in abnormally cold spots in the crust though the requisite pressure hardly explains the petrographical observations. On the other hand the occurrence of bassanite in industrial and experimental work clearly shows the possibility of its metastable formation under wide ranges of conditions".

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REFERENCES

- Boyd, F. R., and England, J. L., 1960, Apparatus for phase equilibrium measurements at pressures up to 50 kilobars and temperatures up to 1750°C.: *Jour. Geophys. Research* v. 65, p. 741-748.
- Bundy, W. M., 1956, Petrology of gypsum-anhydrite deposits in southwestern Indiana: *Jour. Sed. Petrology*, v. 26, p. 240-252.
- Hardie, L. A., 1967, The gypsum-anhydrite equilibrium at one atmosphere pressure: *Am. Mineralogist*, v. 52, p. 171-200.
- Hill, A. E., 1937, The transition temperature of gypsum to anhydrite: *Am. Chem. Soc. Jour.*, v. 59, p. 2242-2244.
- Kelley, K. K., and others, 1941, Thermodynamic properties of gypsum and its dehydration products: U. S. Bur. Mines Tech. Paper 625, 72 p.
- Kennedy, G. C., 1961, Phase relations of some rocks and minerals at high temperatures and high pressures: *Advances in Geophysics*, v. 7, p. 303-322.
- Kitahara, S., and Kennedy, G. C., 1964, The quartz-coesite transition: *Jour. Geophys. Research*, v. 69, p. 5395-5400.
- MacDonald, G. J. F., 1953 Anhydrite-gypsum equilibrium relations: *Am. Jour. Sci.*, v. 251, p. 884-898.
- Palache, Charles, Berman, Harry, and Frondel, Clifford, 1951, *Dana's System of Mineralogy*, v. 2: New York, John Wiley and Sons Inc., 1124 p.
- Palmer, A. R., 1959, Miocene arthropods from the Mohave Desert, California: U. S. Geol. Survey Prof. Paper, v. 294-G, p. 237-280.
- Partridge, E. P., and White, A. H., 1929, The solubility of calcium sulfate from 0° to 200°C: *Am. Chem. Soc. Jour.*, v. 51, p. 360-370.
- Pettijohn, F. J., 1949, *Sedimentary Rocks*: New York, Harper and Bros., 507 p.
- Posnjak, Eugen, 1938, The system $\text{CaSO}_4\text{-H}_2\text{O}$: *Am. Jour. Sci.*, 5th ser., v. 35A, p. 247-272.
- Sharp, W. E., 1962, The thermodynamic functions for water in the range -10 to 1000°C and 1 to 250,000 bars: California Univ. Lawrence Radiation Lab. Rept. 7118, 51 p.
- Stewart, F. H., 1953, Early gypsum in the Permian evaporites of North-eastern England: *Geol. Assoc. London Proc.*, v. 64, p. 33-39.
- Sund, J. O., 1959, Origin of the New Brunswick gypsum deposits: *Canada Mining Metallurgy Bull.* v. 52, p. 707-712.
- Zen, E-An, 1965, Solubility measurements in the system $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$ at 35°, 50° and 70° and one atmosphere pressure: *Jour. Petrology*, v. 6, p. 124-164.