

COMMENTS AND LETTERS TO THE EDITOR

Magnesite Equilibrium from Dissolution and Precipitation: Has It Been Done?

Kittrick and Peryea (1986) recently reported on the stability of magnesite as determined by solution experiments. Their claim to having achieved equilibrium from both dissolution and precipitation is noteworthy since many other attempts have failed.

Wells (1915) was unable to achieve magnesite saturation from dissolution after 61 d under atmospheric CO_2 . Garrels et al. (1960) using an "unusually pure magnesite" were unable to achieve a stable equilibrium pH "because the mineral dissolved so slowly." They found that "filtered, outgassed solutions formed no precipitation for months until, because of evaporation, nesquehoniite, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ formed." Langmuir (1965) has reviewed several attempts to achieve magnesite equilibrium from dissolution and precipitation, all of which failed.

The experimental methods used by Kittrick and Peryea (1986) do not appear to us to be significantly different from methods previously described as unsuccessful, and therefore the data merit closer examination.

Figure 1 shows plots of Mg, pH, and $\text{p}K_f$ values from Table 1 of Kittrick and Peryea (1986). The authors assumed that all data shown were equilibrium values. It appears to us that there are trends of increasing Mg, pH, and $\text{p}K_f$ with time indicating that dissolution was still occurring and equilibrium was not reached. The regressions of Mg, pH, and $\text{p}K_f$ vs. time all had slopes and r values significantly different from 0 at $P = 0.05$, ($n = 32$).

In addition, all three magnesite samples used showed dolomite peaks in the reported XRD patterns. The dissolution of dolomite is at least six times faster than magnesite (Halla, 1963) and was probably contributing Ca, Mg, and alkalinity to solution.

The data from the precipitation experiment also show nonequilibrium trends (plots not given). Space limitations of a Letter to the Editor do not allow us to go into the details of the problems with this experiment. We note that no one has yet synthesized magnesite in aqueous solution below 50°C (Langmuir, 1965), and it is very unlikely that it was achieved in this study. The diagenetic formation of magnesite in soils also has not been documented.

The experiments in the article of Kittrick and Peryea (1986) are complicated by increasing Mg and pH values in the dissolution experiments, dolomite contamination, evaporation (Hooper and Kittrick, 1986), and inconclusive evidence for precipitation. It is our opinion that the data do not confirm that equilibrium was established and the data, if used to calculate the thermodynamic stability of magnesite, may not reflect the true Gibbs free energy of formation for magnesite.

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U.S. Salinity Laboratory,
USDA, ARS
4500 Glenwood Drive
Riverside CA 92501

CHRISTOPHER
AMRHEIN
DONALD L. SUAREZ

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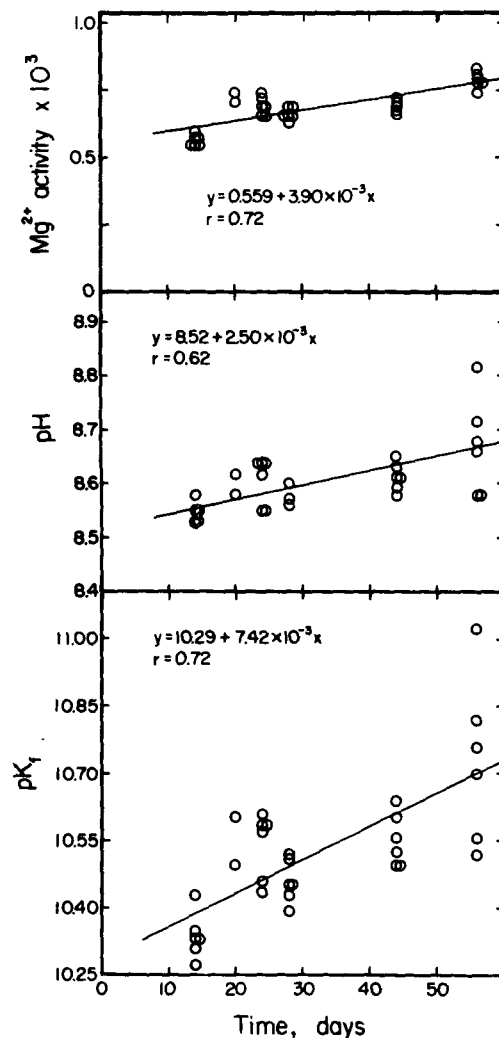


Fig. 1. Mg^{2+} , pH, and $\text{p}K_f$ values vs. time for all dissolution data from Table 1 (Kittrick and Peryea, 1986).

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Reply to "Magnesite Equilibrium from Dissolution and Precipitation: Has It Been Done?"

Drs. Amrhein and Suarez suggest some plausible alternative explanations for the experimental results obtained in our study of magnesite solubility (Kittrick and Peryea, 1986). Our reasons for accepting the role of magnesite as a solubility-controlling agent in our mineral suspensions follow.

Dolomite interference unlikely—We did not measure the concentration of Ca in the equilibrated solutions. The amount of solution that could be separated using the immiscible displacement method permitted only Mg and pH measurements. It must be understood that soluble ion contributions by dolomite or any other impurity are benign so long as the