Mg, using the relationship described earlier, would be expected to have precipitated from a solution with an Mg/Ca ratio of 1 (or greater if Berner’s (1975) or Plummer and Mackenzie’s (1974) data are used). This is near the upper limit of Mg/Ca commonly found in solutions; the ratio is usually lower, including the soil solutions of Marion and Babcock (1977). An 8 mole % Mg calcite requires a Mg/Ca ratio in solution of greater than 4:1, which is certainly greater than commonly associated with soils or major rivers in arid regions (based on either exchangeable ions or solution composition). The occurrence of pedogenic high Mg calcites is thus expected to be rare.

The occurrence of high Mg calcite in modern marine sediments is associated with aragonite (Berner, 1975). This is the result of the increasing stability of aragonite relative to Mg calcite as the Mg content increases. Notably aragonite is not commonly found in soils.

The data of Langmuir (1971) cannot be applied to the discussion of the effects of Mg substitution into calcite on the stability of the calcite phase as was done by Marion and Babcock. The waters described by Langmuir (1971) are derived from the dissolution of low Mg calcite and dolomite. As can be seen in Marion and Babcock’s Fig. 4, the waters taken from Langmuir (1971) were undersaturated. Marion and Babcock indicated a correlation of CaCO₃ activity products with Mg activities in Langmuir’s (1971) data on spring and well waters. Actually, Fig. 4 from Marion and Babcock showed only the spring waters. Clearly, increasing dolomite and calcite dissolution will cause a solution to approach the calcite equilibrium (pKc – pIAP = 0) and the Mg concentration will increase (decreasing pMg). This alone accounts for the slope in (pKc – pIAP) vs. pMg in Langmuir’s data. Only if the waters were supersaturated and high Mg values were correlated with high levels of supersaturation (pKc – pIAP > 0) could this argument be used, i.e., Langmuir’s data in Fig. 4 would have been at equilibrium or supersaturated and it would have to fall on the same line as Marion and Babcock’s. Langmuir’s well water analyses, (not shown by Marion and Babcock) represent waters with longer residence times than the spring waters and, as expected, are closer to equilibrium. These waters show no correlation between pMg and pKc – pIAP.

The only apparent evidence supporting the concept that CaCO₃ solubilities in soils are determined by the Mg content of their calcites is the three data points presented by Marion and Babcock in Fig. 4.

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Literature Cited


Reply to Comment on “The Solubilities of Carbonates and Phosphates in Calcareous Soil Suspensions”

We have not used ion-pair corrected activity products in an inconsistent manner as claimed by Suarez. Most of the solubility products cited in our paper were corrected for ion-pairs. For the carbonate minerals, only the calcite solubility product was not corrected for ion-pairs. For calcite, Langmuir (1968) concluded that the CaCO₃ ion-pair was insignificant in the solution range examined, assuming the presence of CaHCO₃ led to consistent calcite solubility products. Langmuir concluded that calcite solubility could be satisfactorily quantified without including ion-pairs. We used the Langmuir calcite solubility product because we feel Langmuir’s study to be the most definitive to date.

We agree with Suarez that the solutions were probably not at equilibrium with the solid phases. Bicarbonate concentrations continued to increase, but at an ever-decreasing rate, over the 41 days of the experiment (Fig. 1; Marion and Babcock 1977).

Our statement that “evidence from the literature indicates that Mg substitution can account for the reported soil CaCO₃ activity products” is certainly true for the Panache and Clear Lake soils. Magnesium substitution in soil calcite up to 8% is known to occur under pedogenic conditions (St. Arnaud and Herbillon, 1973). High Mg-calcite may well be rare as the unpublished work of Suarez indicates; but, this does not refute our statement.

Suarez has misinterpreted our use of the Langmuir (1971) data on carbonate solubility. We utilized data from both spring and well waters issuing from limestone bedrock; in particular, waters issuing from dolomite bedrock were not used. Because most of the Suarez arguments depend on a misinterpretation, they cannot be logically answered.

Magnesium substitution can account for considerable variation in calculated calcite activity products (Fig. 3; Marion and Babcock, 1977). But clearly more work will be necessary before the general significance of Mg substitution in soil calcite is established; in particular, direct measurement of Mg substitution in soil calcite would be most useful.

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Literature Cited