COMMENTS AND LETTERS TO THE EDITOR

Comments on “Solution Sulfate Chemistry in Three Sulfur-Retentive Hydrandepts”

The presentation of thermodynamic stability diagrams to explain ionic solubility controls has been criticized because the axes are often dependent (Neal, 1988). This dependence may cause spurious correlation and misinterpretation of the data. An example of highly dependent axes can be found in Fig. 1 of Wolt et al. (1992) entitled “Soil solution ion activities relative to stability lines for Al-hydroxysulfate minerals and gibbsite”. The Y axis is pAl + pOH + pSO_4. The authors explained that pAl was estimated assuming the solubility of cryptocrystalline gibbsite: pAl = 3pH − 9.2. If one substitutes 3pH − 9.2 for pAl and 14 − pH for pOH, the Y axis reduces to 2pH + pSO_4 + 4.8. Figure 1, then, is simply a plot of the sum of two variables vs. the sum of the same two variables plus 4.8. A linear relationship is obviously unavoidable. Conclusions about the data should not be drawn from this particular plot.

This comment is not intended to detract from the significance of the data itself or the authors’ other conclusions. Received 28 Apr. 1992.

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Don Ross correctly observed the interdependence of the X and Y axes for the stability diagram (Fig. 1) appearing in Wolt et al. (1992). We clearly recognized this interdependence and its influence on the representation of the data when we stated with reference to Fig. 1, “Data for solutions fall along the line fixed by gibbsite from which Al\(^{3+}\) activity was estimated.” As we described, the lines in Fig. 1 that represent Al-hydroxy-sulfate mineral stability are the reference K_{sa} rearranged to fit the axes and, thus, are fixed for given values of K_{sp}, T, and p. Gibbsite was included in the diagram through addition of [2pH + pSO_4] to the reference K_{sa}. The resulting stability diagram allows consideration of how the solid-phase mineral controlling soil solution Al\(^{3+}\) activity (cryptocrystalline gibbsite in this instance) influences the apparent over- or undersaturation of soil solution with respect to various Al-hydroxy-sulfate minerals. The interdependence of the axes is realized when one observes shifts in pAl on the basis of the solid-phase mineral assumed to control soil solution Al\(^{3+}\) activity, as we demonstrated for the sensitivity analysis of the negative logarithm of the ion activity product (pIAP) for basaluminite. A stability diagram of this type is useful for gaining intuitive insights regarding mineral stability relationships. One is unable to draw conclusions on the basis of the diagram alone, however, because of the underlying assumptions on which this figure is based (one of the points of our presentation). Recognition of the nature of the stability diagram presented and our stated assumptions underlying its construction, allowed us to observe that “alunite and especially basaluminite could be stable solid-phase components in conjunction with gibbsite when [2pH + pSO_4] < 15.5°”. Our thanks to Dr. Ross for pointing out the need to clarify the use and limitations of data presented in this manner.

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