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EQUILIBRIA AMONG VARIABLE- COMPOSITION MINERALS AND AQUEOUS SOLUTIONS UNDER HYDROTHERMAL CONDITIONS

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ABSTRACT

Equilibrium phase relations among stoichiometric mineral assemblages and aqueous solutions are usually interpreted using logarithmic activity diagrams. The method has limited utility however, because many of the assemblages found in nature contain minerals with highly variable composition. Using a model which considers ideal mixing of atoms on completely or nearly homological sites in silicate structures, examples of modified activity diagrams are constructed for phase relations involving clay., epidote and chlorite.

INTRODUCTION

Equilibrium phase relations among mineral assemblages and aqueous solutions are commonly interpreted using logarithmic activity diagrams. The technique generally works quite well with minerals whose compositions depart slightly or none at all from strict stoichiometry. However, minerals which exhibit high compositional variability such as garnets, epidotes, illites, chlorites, montmorillonites, glauconites and mired-layer clays comprise the bulk of assemblages found in nature. This severely limits the usefulness of the method.

The simplest, albeit naive, approach to circumvent this constraint is to represent these "aggregates" in terms of well-characterized stoichiometric minerals that display some thermodynamic and chemical resemblance to the former. This has been found to be wanting and oftentimes misleading. Various workers (e.g. Tardy and Garrels, 1974; Nriagu, 1975; Mattigod and Sposito, 1978) have attempted to estimate the thermochemical properties of these minerals with varied results. Others have adopted more elaborate methods such as using solid or regular solution models (Tardy and Fritz, 1981; Stoessell, 1979; 1981). An alternative approach introduced in recent years considers ideal mixing of atoms on completely or nearly homological sites in the mineral structures (Aagaard and Helgeson, 1983; Walshe and Solomon, 1981; Bird and Helgeson, 1980).

Each of the above treatments has its own strength, limitations and theoretical drawbacks. Because of its simplicity and ease of handling, the last-mentioned approach is adopted here to show by simple examples, how phase relations involving variable composition minerals and aqueous solutions can be represented in stability diagrams.

ACTIVITY-COMPOSITION RELATIONS

The basic result from the model is a set of mixing equations which takes into account compositional variation on tetrahedral, octahedral and exchange sites in the silicate structures. The equation for the activity of the $\underline{i}$th thermodynamic component (a_i) in a solid solution is given by (Aagaard and Helgeson, 1983)

$$a_i = k_i \prod_s \prod_j a_{j,s}^{\nu_{s,j,i}}$$

where k_i is a constant which normalizes the activity of the pure end member component to unity; $a_{j,s}$ stands for the activity of the $\underline{j}$th atom on the $\underline{s}$th homological sites in the solid solution; and $\nu_{s,j,i}$ is the stoichianetric number of the sites occupied by atom $\underline{j}$ in a mole of component $\underline{i}$. In the limit of ideal mixing of atoms in the respective sites, and on the basis of the standard states defined by Aagaard and Helgeson (1983), the $a_{j,s}$'s pass into mole fractions, $X_{j,s,i}$.

EQUILIBRIA INVOLVING CLAYS

By combining the activity-composition relations derived from ideal mixing of atoms in homological sites and empirical data, Aagaard and Helgeson (1983) were able to construct an approximate logarithmic activity diagram involving illites, montmorillonites, and mixed-layer clay.. They chose muscovite, pyrophyllite, paragonite and margarite as the end member. Giggenbach (1983a,b) on the other hand, has shown that dioctahedral clays can be adequately represented (neglecting trace-element components) in terms of pyrophyllite, alkali mica and celadonite. Based on this consideration, he was able to delineate stability rekations of these layer silicates and aqueous solutions as a function of $\underline{m}$, the number of aluminium atoms substituting for silicon on the tetrahedral sites; $\underline{X_j}$ the fraction of occupancy in the

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exchange sites and c, the number of divalent cations on octahedral sites.

Except for slight changes, Giggenbach's (1983b) approach, combined with the thermodynamic data given by Helgeson, et al (1978; 1981) for the stoichiometric minerals and aqueous species, respectively, were used to generate figs.1 and 2. Overwhelming evidence (Reesman, et al, 1969; Day, 1976; May, et al, 1979; Perkins, et al, 1979; Hemley, et al, 1980) show that diaspore is the most stable aluminium hydroxide phase under the conditions depicted in figs 1 and 2, and was subsequently adopted. The thermodynamic data for the unspecified K-feldspar (Helgeson, et al, 1978) were used, which could represent microcline, adularia or andesine depending on the given conditions. All the stability fields of other dioctahedral phases like phengite, beidellite and celadonite were omitted to simplify the diagrams. In any event, these are not quite as important in hydrothermal environments. The criteria for constructing the stability limits involving the variable-composition minerals adopted by Giggenbach (1983b) were followed here.

Qualitatively, there is not much change in the stability fields of the various clays as temperature rises from 25°C (fig.4, Giggenbach, 1983b) to 200°C, except for the expansion of the illite field with increasing temperature relative to that of montmorillonite. This is consistent with observation (see Browne (1978) for a survey of alteration minerals in geothermal fields).

Since quartz saturation usually prevails in moderate to high temperature geothermal waters, it is interesting to observe the sequence of alteration minerals as a function of log (a_{K^+}/a_{H^+}). Typical geothermal waters would plot near the K-feldspar-illite or interlayered illite-montmorillonite-K-feldspar boundary, but montmorillonite is favored by low K+-activity or pH. *Very* low pH or K+ favors quartz supersaturation (but still undersaturated with respect to amorphous silica) and metastable reactions (Hemley, et al, 1980), and it is easy to see from the diagram that pyrophyllite could be associated with an argillic alteration assemblage at these temperatures.

STABILITY OF EPIDOTE

In most geologic situations, epidote can be regarded as a solid solution of clinozoisite $[Ca_2Al_3Si_3O_{12}(OH)]$ and "epidote" $[Ca_2FeAl_2Si_3O_{12}(OH)]$ (Bird and Helgeson, 1980). By assuming ideal intracrystalline mixing of atoms in the

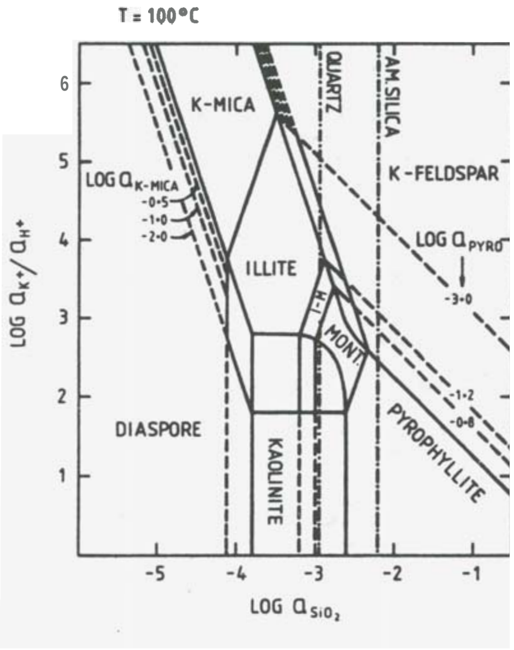

Fig.1. Logarithmic activity diagram involving illite, montmorillonite and interlayed illite-montmorillonite as well as stoichiometric minerals in the system $K_2O-Al_2O_3-SiO_2-H_2O$ at 100°C. Stability "boundaries" adopted are those by Giggenbach (1983a,b). See text.

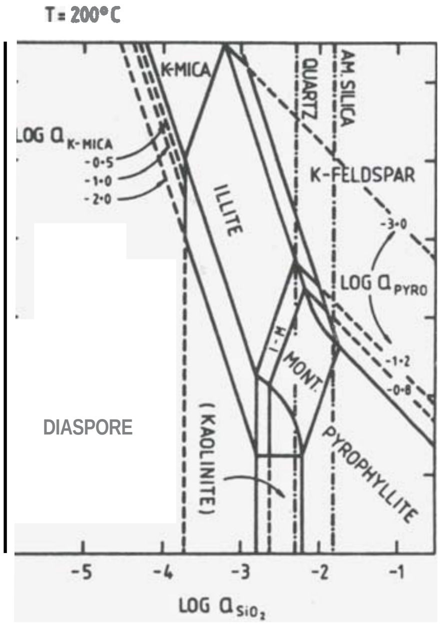

Fig.2. Same as Fig.1 except that T = 200°C

octahedral sites M(1) and M(3) in epidote solid solution, Bird and Helgeson (1980) established appropriate activity expressions for the components as functions of mole fraction., X_i, and a temperature-dependent disordering parameter.

The thermodynamic consequences of this treatment are shown in fig.3. It can be seen that representing epidote as pure clinozoisite ($X_{ep} = 0$) results in an unrealistically small stability field for the mineral (striped area). Increasing the epidote component mole fraction and taking into account intrasite mixing successively enlarge the stability field of the solid solution. One can also regard K-mica as a component of say, illite, which can undergo changes in activity as mentioned earlier. In which case then, an illite-epidote coexistence field would be delineated. Rather than introducing mote realism at the expanse of clarity of exposition, this refinement is not included. The last point does justify the commonly observed illite-epidote or illite-epidote-K-feldspar (plus quartz, of course) in geotherma, environments at this temperature.

The extent of the prehnfte stability field is illusory. In most instances, the ratio a_{Ca++}/a^2_{H+} is also controlled by calcite or anhydrite saturation, so the commonly associated mineral with epidote is calcite or anhydrite rather than prehnite. Only in exceptional instances will prehnite be observed as an alteration product.

SOME CHLORITE PHASE RELATIONS

chlorite is another ubiquitous alteration product which displays a highly variable composition. Recently, a six-component chlorite model was introduced (Walshe and Solomon, 1981) but with limited success. Part of the shortcoming could be due to absence of reliable thermochemical data for some components or to the inherent artificiality in defining the constitutive components. Therefore, instead of adopting this model, a more pragmatic approach is used here, wherein the activity of the clinochlore component of chlorite is varied successively without regard to the nature of alltheother components. This procedure corresponds to solid solution formation.

Fig.4 shows the mineralogic phase relations in the system $MgO-K_2O-Al_2O_3-SiO_2-H_2O$ at 300°C and quartz saturation. It can be observed that representing chlorite as stoichiometric clinochlore results in some phase relations quite contrary to observations. For example, a coexistence curvey of chlorite (clinochlore) and a k-mica bearing mineral (e.g. illite) is nonexistent. Varying the activity of clinochlore however, significantly enlarges the chlorite stability field; as a result, a chlorite-illite (k-mica) or even possibly chlorite-illite(k-mica)-biotite (phlogopite) assemblage could exist at this temperature.

Expansion of the k-mica field as a consequence of solid solution formation towards the clinochlore field is not as dramatic though, as shown for $a_{k-mica} = 0.1$. Phlogopite as used here represents biotite, which should be regarded as a solid solution (Beane, 1974), but this aspect is not considered here, again, for clarity.

DISCUSSION

These examples show that stability fields expand consequent to the formation of a solid solution. This is to be expected if one views the alteration process in the thermodynamic sense. *An* original igneous assemblage can be regarded as a complex mixture of thermodynamic components in internal equilibrium. Contact with a hydrothermal solution amounts to removal of some internal constraints in the system. In the process, the various campositional parameters readjust as the perturbed system seeks to minimize its free energy. When spatial, kinetic and compositional factors inhibit the formation of distinct phases, instead, polyphase aggregates, solid solutions and metastable phases are produced.

While the examples show that the treatment is an improvement over previous methods, it should be *regarded* as just a reasonable approximation to a complex reality. In substances as complex as silicates, ideal mixing is expected to be an exception rather than the rule. What are considered homological sites (exchangeroctahedral and tetrahedral) often depart significantly from being equivalent. Different atom by sheer size alone perturb differently the silicate structural framework. And when changes in valence are involved, local electrostatic imbalance is created which, formally, should be accounted for.

No wonder the various proponents are cautious of generalizing the method yet.

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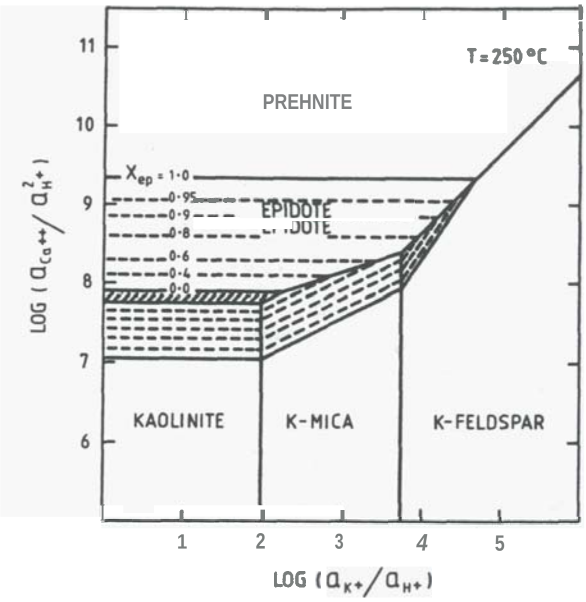

Fig.3. Phase relations in the system $CaO-K_2O-Al_2O_3-SiO_2-H_2O$ at 250°C and saturated water vapour pressure which take into account compositional variation and order-disorder in epidotes. Dotted lines indicate equilibrium boundaries for various mole fractions, Xep, of epidote [$Ca_2FeAl_2Si_3O_{12}(OH)$] in the epidote-clinozoisite solid solution calculated using the equations of Bird and Helgeson (1980). The small shaded area represents the stability field for stoichiometric chlinozoisite.

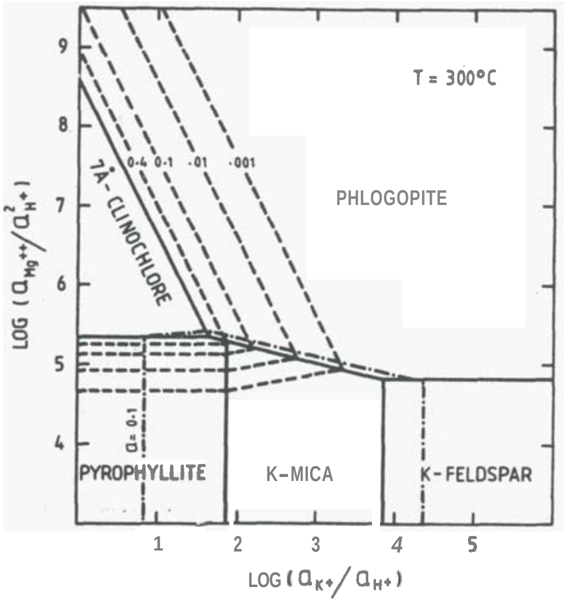

Fig.4. Phase relations in the system $MgO-K_2O-Al_2O_3-SiO_2-H_2O$ at 300°C and saturated water vapour in the presence of excess quartz showing the thermodynamic consequences of variation of clinochlore activity in chlorite. Dotted lines indicate equilibrium boundaries as a function of clinochlore activity.

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