



The standard thermodynamic properties of vermiculites and prediction of their occurrence during water–rock interaction



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ABSTRACT

The standard thermodynamic properties (ΔG_f° , ΔH_f° , S° , and V°), at 298.15 K, 1 bar, of 16 vermiculites and their heat-capacity coefficients were computed in this research following the approach of Wolery and Jove-Colon (2007). In this way, data consistent with those of other sheet silicates contained in the thermodynamic database data0.ymp.R5 of the EQ3/6 software package were obtained.

Although the uncertainty of these data is too high to investigate exchange reactions involving vermiculites, they can be profitably used to predict the conditions of vermiculite formation during weathering. The shallow groundwaters interacting with granitoid and gneissic rocks and overlying soils, from an area of the Sila Massif (Calabria Region, Italy), were taken into account for an example of application. Results of speciation–saturation calculations for these waters show that: (i) in general, production of vermiculites hosting Mg^{2+} and Ca^{2+} ions in the interlayer sites is favoured with respect to generation of vermiculites whose interlayer sites are occupied by Na^+ and K^+ ions; (ii) the possibly forming solid phases (all metastable with respect to Mg–Fe–vermiculite) are kaolinite, Mg–Al–vermiculite, and Mg–Mg–Fe–vermiculite, in order of increasing pH values. In detail, kaolinite/Mg–Al–vermiculite coexistence occurs at pH close to 6.7, whereas Mg–Al–vermiculite/Mg–Mg–Fe–vermiculite coexistence occurs at pH close to 7.3.

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1. Introduction

Weathering of biotite, a major source of K in soils, is a very important process affecting soil fertility. Therefore, a great number of contributions, comprising both field studies and laboratory experiments, have swelled the literature pertaining to this subject (e.g., Wilson, 2004 and references therein as well as Balogh-Brunstad et al., 2008; Föllmi et al., 2009; Hopf et al., 2009; Sokolova et al., 2010; Bhatti et al., 2011; Arocena et al., 2012).

It is well established since 70 years at least that biotite weathering is a relatively quick process. Indeed, it was recognized long ago that biotite is a *moderately stable* mineral during weathering, being positioned between hornblende and potash feldspar in the *mineral-stability series in weathering* of Goldich (1938), and that *biotites decay more rapidly than muscovites* (Jenny, 1941) among micas. These early findings were recently confirmed and quantified through laboratory measurements of biotite dissolution rates (Acker and Bricker, 1992; Turpault and Trotignon, 1994; Kalinowski and Schweda, 1996; Malmström et al., 1996; Malmström and Banwart, 1997; Taylor et al., 2000; Samson et al., 2005; Haward et al., 2011), that indicated occurrence of both early removal of interlayer

K^+ ion at any pH and of non-stoichiometric dissolution, as well as a considerable influence of redox potential, with dissolution rates much higher under oxidizing conditions than under anoxic conditions.

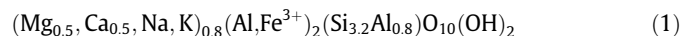
Previous studies also recognized that biotite weathering proceeds through different pathways, depending upon a number of factors, chiefly comprising climate, weathering conditions, rock composition and chemistry of altering fluids, thus leading to the production of distinct secondary mineral phases. These include hydrobiotite, chlorite/vermiculite, vermiculite, smectite, trioctahedral illite, kaolin-group minerals, gibbsite, and iron and titanium oxides.

Vermiculitization is the simplest pathway of biotite weathering as it involves exchange of interlayer K ions of biotite for ions of the aqueous solution, without any structural rearrangement (Barshad, 1948). In natural systems, vermiculitization of biotite often implies, in a preliminary step, the production of hydrobiotite, a regularly interstratified biotite–vermiculite with a basal spacing of ~ 24 Å (Coleman et al., 1963; Wilson, 1970), although it may alternatively proceed through depletion of K from some preferred layers, which are adjacent to other K-undepleted layers (Banfield and Eggleton, 1988). Vermiculitization is often preceded by oxidation of octahedral ferrous ion, typically determining the formation of interlayer oxides, either amorphous or crystalline (e.g., Walker, 1949; Farmer et al., 1971; Gilkes et al., 1972).

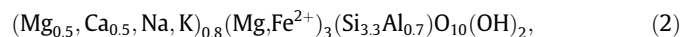
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According to Essington (2005), vermiculites are 2:1 phyllosilicates whose layer charge originates chiefly in the tetrahedral layer, due to isomorphic substitution of Al^{3+} for Si^{4+} , and varies between ca. 0.6 and 0.9 per formula unit, on the basis of 22 negative charges. Adopting a 0.8-layer charge, the idealized formulas of dioctahedral vermiculites and trioctahedral vermiculites are:



and



respectively. In fact: (i) Mg^{2+} or Fe^{2+} ions are generally present in the octahedral sites of natural vermiculites, though substitution by Al^{3+} and Fe^{3+} ions occurs to some extent, and (ii) interlayer sites are usually occupied by Mg^{2+} ions although Ca^{2+} and less commonly Na^+ and K^+ ions are also present (Deer et al., 1992). The interlayer position may also be partly occupied by other cations, such as Al^{3+} ion (Aurousseau et al., 1983), but this possibility is not considered in this work.

As reported by Essington (2005), vermiculites are expandable and their internal surfaces are accessible to water molecules and other ions and molecules present in the bathing solution. Charge-satisfying, interlayer cations are therefore easily exchangeable. The *d*-spacing of vermiculites depends on the interlayer cation and varies from 1.0 nm, when interlayers are saturated by K^+ ion, to 1.4–1.5 nm upon interlayer saturation by Mg^{2+} or Ca^{2+} ions. The specific surface of vermiculites, 600–800 $\text{m}^2 \text{g}^{-1}$, is similar to that of smectites. However, the CEC of vermiculites, 100–200 meq/100 g, is higher than that of smectites, owing to the greater layer charge, and is in the uppermost range of inorganic minerals.

A thermodynamic determination of sufficient precision and accuracy is always preferable with respect to an estimation, but thermodynamic properties of vermiculites, similar to many other clay minerals, are difficult to be measured with sufficient precision and accuracy by means of experimental methods such as calorimetry, HF dissolution reactions, and solubility determinations. Moreover, a large number of experiments would be necessary, due to the variable composition of clay minerals. Therefore, it is permissible to use the semi-empirical, semi-theoretical techniques which were developed for estimating the standard Gibbs free energy of formation, ΔG_f° , enthalpy of formation, ΔH_f° , third-law entropy, S° , and isobaric heat capacity, C_p . An excellent discussion on these estimation techniques is given by Nordstrom and Munoz (1994). In particular, a comprehensive approach was developed by Wolery and Jove-Colon (2007) to obtain standard thermodynamic¹ data for several sheet silicates (but not for vermiculites) to be inserted into the thermodynamic database of the EQ3/6 software package (see Section 3.1).

This study intends, first, to adopt the approach of Wolery and Jove-Colon (2007) to estimate the standard thermodynamic properties of different vermiculite compositions which can be considered as endmembers of solid solutions occurring in natural systems. In a second step, the data obtained in the previous step are used to obtain indications on the conditions of vermiculite formation during weathering, referring to shallow groundwaters coming from an area of the Sila Massif (Calabria Region, Italy). Soils of the study area are developed over granitoid and gneissic rocks and contain a considerable amount of chloritized biotite and its weathering products, including vermiculite, as discussed in the

¹ Following Johnson et al. (1992), the standard state convention adopted for solid and liquid phases is the pure phase at all temperatures and pressures. For gases, it is the hypothetical gas at 1 bar and any temperature. For aqueous solutes it is the hypothetical 1 molal solution referenced to infinite dilution at any pressure and temperature.

Section 3.2.

The results of this study can be transferred to other areas in which vermiculite forms through weathering of biotite contained in crystalline rocks, a fact which makes this contribution of great interest, due to the frequent worldwide occurrence of such rocks. Prediction of clay mineralogy (e.g., formation of vermiculite instead of other clay minerals) has practical implications; in fact, since vermiculite is characterized by the highest CEC values among clay minerals (see above), its formation may have a strong impact on nutrient availability in soils and removal of toxic ions from soil waters.

2. Methodology

2.1. Calculation of the standard thermodynamic properties of vermiculites

The standard thermodynamic properties of 16 vermiculites were computed in this work. Each of these vermiculites is indicated with a name in which the first chemical element identifies the exchangeable cation occupying the interlayer sites (Me = Na, K, Mg, and Ca), whereas the second element and the third one (if any) represent the cations in the octahedral sites. The four considered vermiculite groups are Me–Fe–vermiculites, Me–Al–vermiculites, Me–Mg–Al–vermiculites, and Me–Mg–Fe–vermiculites.

As anticipated in the Introduction, the standard Gibbs energy of formation (ΔG_f°) of vermiculites, at the reference temperature, pressure of 298.15 K, 1 bar, was estimated by means of the method of Wolery and Jove-Colon (2007), deriving from the algorithm proposed by Tardy and Garrels (1974). The linear approach of Tardy and Garrels (1974) is based on the assumption that the Gibbs free energy of a sheet silicate is the sum of the product of the Gibbs free energies of each “silicated” oxide and hydroxide components² and their stoichiometric coefficient (v_i) in the phyllosilicate, as expressed by the following equation:

$$\Xi_j^\circ = \sum_i v_i \cdot \Xi_i^\circ \quad (3)$$

in which Ξ_j° and Ξ_i° represent any thermodynamic property or parameter in the *j*th sheet silicate and in the *i*th “silicated” oxide or hydroxide component, respectively.

Wolery and Jove-Colon (2007) extended the linear approach of Tardy and Garrels (1974) considering not only the silicated components SiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MgO , CaO , Na_2O , K_2O , H_2O , and $\text{Mg}(\text{OH})_2$, which constitute the phyllosilicates layers, but also the silicated exchangeable components MgO , CaO , Li_2O , Na_2O , K_2O , H_2O , pertaining to the interlayer sites. Wolery and Jove-Colon (2007) provides the standard Gibbs free energy of both type of components, which were used to calculate the ΔG_f° of vermiculites at reference T, P, using Eq. (3).

In addition, following the guidelines of Wolery and Jove-Colon (2007), some reference reactions were also employed to calculate the ΔG_f° of vermiculites, imposing that the Gibbs free energy of reaction is equal to zero as indicated by the following equation:

$$\Delta \Xi_r^\circ = \sum_i v_i \cdot \Delta \Xi_i^\circ + \sum_j v_j \cdot \Delta \Xi_j^\circ = 0 \quad (4)$$

where $\Delta \Xi_r^\circ$ stands for any thermodynamic property or parameter of reaction and v_i and v_j are negative for reactants and positive for products.

Reference reactions for Me–Fe–vermiculites involve either

² Tardy and Garrels (1974) defined the Gibbs free energy of silication (in sheet silicates) as the difference between the Gibbs free energy of a “silicated” oxide component (as determined in their regression) and the Gibbs free energy of the corresponding stable oxide phase.

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