Solution Chemistry of Fragipans—Thermodynamic Approach to Understanding Fragipan Formation

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Abstract

Most of the pedological interpretations and speculations about fragipan development have focused primarily on macro- and micromorphological descriptions and physical, chemical, and mineralogical characterizations of the solid phase. It is surprising that, although fragipans are some of the least-changing soil horizons over time (restricted influxes-outfluxes due to their dense and brittle character, limited biotic activity), no attempt has been made to describe them thermodynamically. Steadystate compositions of soil solutions in contact with fragipan constituents should be valid indicators of fragipan evolution. Furthermore, the development of thermodynamic relationships describing solution-mineral interactions in fragipan and overlying nonfragipan horizons should be useful in the identification of mineral weathering trends typifying a fragipan pedogenic environment. This chapter discusses such a thermodynamic approach used in a study of loess-derived Fragiuudalfs underlain by various lithologies in Kentucky. Solution chemistry, reactive fraction, and mineralogical composition evaluations of fragipans in these soils supported the hypothesis of a Si-rich amorphous aluminosilicate binding agent with a Si molar fraction ranging from 0.58 to 1.00. This amorphous aluminosilicate coating appears to be the initial product of feldspar weathering. It is proposed that precipitation of amorphous SiO$_2$ on the amorphous aluminosilicate surface from Si-saturated solutions during desiccation periods and subsequent irreversible induration leads into the formation of fragipans. The intensity of these processes is controlled by site geomorphological characteristics that determine the degree of fragipan development.

Pedologists in their long struggle to understand the processes responsible for fragipan formation have concentrated their efforts on morphological, physicochemical, and mineralogical characterizations of the solid phase (Knox, 1957; Yassoglou & Whiteside, 1960; Grossman & Carlisle, 1969; Daniels et al., 1966; Buntley et al., 1977; Hutcheson & Bailey, 1964; Lozet & Herbillon, 1971; Hallmark & Smeck, 1979; Steinhardt & Franzmeier, 1979; Norton et al., 1984). These characterizations have provided a wealth of information that has helped explain a significant part of fragipan evolution processes. In the course of these efforts, little (Karathanasis, 1987a, b) or no attention was paid to the medium surrounding and interacting with the solid phase, the soil solution, from which some of the binding constituents may have originated. After all regardless of the mode of fragipan evolution, the interstitial soil solution should have played a significant role, as it has in all pedogenic processes.

Under the relatively constant temperature and pressure conditions of the earth's surface, most of these changes are triggered by fluctuations in the activities of solutes filling the interstices between the mineral particles. Over relatively long periods of time, the composition of the soil solution in a given soil system is the result of reactions toward a steady state of the more reactive minerals, as they are being modified by solutes entering the soil with surface or groundwater inputs and solutes produced from biological and evaporative processes (Brinkman, 1979; Sposito, 1985). Because of the continuous interaction between mineral and solution phases, at any given time, the composition of the soil solution reflects the nature and direction of reactions of the most reactive minerals toward attaining a steady state. At the invariant condition of the steady state, the true solution composition may be characteristic of a stable or near stable mineral assemblage depending on kinetic limitations. The near stable (approaching equilibrium) condition is more attainable in soil systems in which the soil solution...
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14.1 Introduction

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The physical chemistry of soil is determined by a large, variably charged interface between the many solid phases and the soil solution. This interface continuously exchanges ions supplied or withdrawn via flowing water and soil organisms. Soil biology is dominated by intricate meshes of plant roots and numerous decomposers. The relationships between the different approaches to study soil processes are shown diagrammatically in Figure 1.1. Question 1.4 A silt-textured soil profile in a dry region has a water table within 1 m of the soil surface and has a white crust on the soil surface. Chemical thermodynamics is the part of thermodynamics that concerns the physical change of state of a chemical system following the laws of thermodynamics. The thermodynamic properties of individual phases can be used for evaluating their relative stability and heat evolution during phase transformations or reactions. Traditionally, one of the most common applications of chemical thermodynamics is for the construction and interpretation of phase diagrams. The thermodynamic quantities that are most frequently used in material sciences are the enthalpy, in the form of the heat solution. First we must find the amount of heat released by the ethane. To do this, we calculate the number of moles of ethane gas using the ideal gas equation and multiply the molar heat of combustion by the number of moles. \[ \Delta H_{\text{combustion}} = 1437.17 \text{ kJ/mol} \]

Use \( \Delta H \) of formation (HF) for each of the chemicals involved in the reaction found in a standard table or reference book. \[ \Delta H_F \text{H}_2 \text{O} = -285.83 \text{ kJ/mol} \] \[ \Delta H_F \text{O}_2 = 0 \text{ kJ/mol} \] \[ \Delta H_F \text{H}_2 = 0 \text{ kJ/mol} \]

\[ \Delta H_{\text{rxn}} = \sum (\Delta H_F \text{water}) - (\Delta H_F \text{O}_2 + 0 \text{ kJ/mol}) - \Delta H_F \text{H}_2 + 0 \text{ kJ/mol} \]

Q9. Using standard thermodynamic values, calculate the enthalpy of the reaction of the combustion of methane gas with oxygen gas to form carbon dioxide and liquid water. Solution. Chemical Equation: \( \text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l) + \text{heat} \)

These conditions are closely met in fragipan horizons because of their brittleness, high bulk density, and limited permeability and biological activity. Therefore, fragipans present some of the best pedological systems that can be successfully modeled thermodynamically. Nevertheless, the application of classical thermodynamics to soil systems has several inherent limitations. Soils, even at steady-state conditions, are open systems in which energy and matter influxes and outfluxes are just sufficient for maintaining a balance in the properties of the system (Smeeck et al., 1983). This steady state, however, may or may not represent the equilibrium state due to kinetic limitations.

The adequacy by which a natural soil system can be approximated by an equilibrium model will depend on the extent to which the natural system resembles an equivalent closed system. Even at a close match between natural and ideal systems, however, it should be emphasized, that the thermodynamic approach can only predict what components would be present under equilibrium conditions. In spite of the limitations, idealized equilibrium models mimicking selected natural soil systems can provide valuable insights into the nature, prevalence, and direction of weathering processes characteristic of specific pedogenic environments (Stumm & Morgan, 1981; Sposito, 1986; Kittrick, 1977; Nordstrom et al., 1979).

Bearing these in mind, an attempt was made to use a soil solution thermodynamic approach in some Kentucky soils with fragipan horizons with the hope that the information obtained will help to:

1. Establish soil solution and mineralogical composition relationships in fragipan and nonfragipan horizons.
2. Identify mineral weathering trends that could explain morphological, physicochemical, and mineralogical differences between horizons with and without fragic properties.
3. Determine the nature and composition of possible fragipan binding agents using soil solution thermodynamic principles.

The study included comprehensive solid and solution phase characterizations of 17 fragipan and 10 nonfragipan horizons. The nonfragipan horizons were sampled from the same or similar pedons and were used as comparison controls. Thermodynamic relationships developed from these characterizations were used to assess the importance of mineral and solution components involved in processes leading to fragipan formation.