STABILITIES OF THREE-LAYER PHYLLOSILICATES RELATED TO THEIR IONIC-COVALENT BONDING

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ABSTRACT

The anhydrous structures of three-layer phyllosilicates are destroyed by heating, as in differential thermal analyses, over a range of temperatures starting from about 775°C, mean temperature for pyrophyllite, and rising to about 1075°C, a mean temperature for biotite. Parallel to the trend of increasing temperature of stability (and destruction) is an increased ratio of substituted Al for Si in the tetrahedral layers and, in some occurrences, of Mg for Al in the octahedral layers. These substitutions increase the degree of ionic bonding (and decrease the covalent bonding) within the oxygen framework. The electronegativity difference between the cation and oxygen increases as Al substitutes for Si, and Mg for Al. Increase in ionic character of a compound is compatible, from chemical considerations, with increase in thermal stability and susceptibility of the compound to alteration by water.

The principle illustrated by the phyllosilicates applies likewise to mineral groups of other silicate structure, such as the anorthite–albite series, the forsterite–fayalite series, and others.

INTRODUCTION

WITHIN the three-layer phyllosilicates an interrelationship occurs between the ratio of ionic to covalent bonding in them and such of their properties as temperatures of thermal destruction, sequence of resistance to weather, and some aspects of solubility. Thus, it appears that the ionic-covalent character of bonding in these phyllosilicates is basic to, and exerts a controling effect on, their relative stabilities. Cursory examination of certain other closely related groups of silicates suggest that the same principle governs their relative stabilities.

RELATIONSHIP BETWEEN THERMAL STABILITY AND COMPOSITION

From experiments on static heating, followed by X-ray diffraction analyses, of three-layer clays derived from parent rocks containing, or alternatively, others relatively free from mica, it was observed that the maximum temperature of destruction of the clay minerals was higher in those clays having a mica heritage, i.e., clays displaying mica-derived properties, than in clays from non-mica parent materials (Tlapek, 1961). This observation led to a survey of the literature for the temperatures of destruction, or "maximum thermal stability", of additional clay minerals,

TABLE 1.—MAXIMUM TEMPERATURES OF STABILITY

Mineral	Temp. Range	Mean	Reference
Dioctahedral Phyllosilicates, Al Dominant Octahedral Cation			
Muscovite	940°–980°C	960°C	Roy, 1949
Illite (8 samples)	890°–915°C	897°C	
3 samples	890°–915°C	902°C	Grim and Rowland, 1942
5 samples	890°–900°C	896°C	Kauffman and Eillin, 1950
Montmorillonite			
(25 samples)	790°–910°C	858°C	
5 samples	850°–910°C	880°C	Bradley and Grim, 1951
8 samples	820°–885°C	853°C	Earley, Osthaus and Milne, 1953
12 samples	820°–900°C	870°C	Grim and Rowland, 1942
10 samples	790°–880°C	832°C	Page, 1943
Pyrophyllite	700°–850°C	775°C	Mackenzie, 1957
Dioctahedral Phyllosilicates, Fe^{+++} Dominant Octahedral Cation			
Glauconite			
(10 samples)	910°–970°C	945°C	Warshaw, 1957
Nontronite			
(2 samples)	850°–880°C	865°C	
	850°C		Bradley and Grim, 1951
	880°C		Mackenzie, 1957
Trioctahedral Phyllosilicates, Mg Dominant Octahedral Cation			
Biotite	1000°–1100°C	1075°C	Roy, 1949
Phlogopite	920°–950°C	935°C	Roy, 1949
Saponite (3 samples)	840°–904°C	875°C	
	904°C		Faust, 1951
	840°C		Faust and Murata, 1953
	880°C		Mackenzie, 1957
Talc	830°–950°C	890°C	Graf, Wahl and Grim, 1962

and thence to those of three-layer phyllosilicates in general. Data on the range of, and mean temperatures of maximum thermal stabilities of three-layer phyllosilicates are assembled in Table 1.

The maximum temperatures of stability are shown graphically in Fig. 1, being separated into dominant di- and tri-octahedral mineral types, and according to the dominance of Al, Fe+++, or Mg as the octahedral cation. They are plotted horizontally in terms of approximate Al : Si ratios in their tetrahedral layers. The vertical length of each bar shows the range
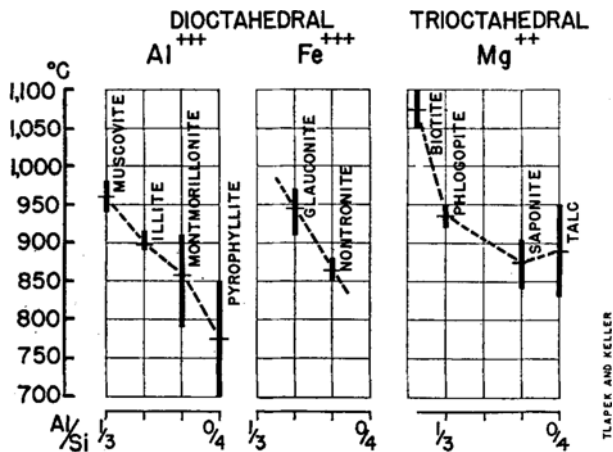

FIGURE 1.—Temperatures of destruction, or maximum temperatures of stability, of the anhydrous structures of three-layer phyllosilicates.

of maximum thermal stability reported on that mineral, and the mean of the temperature of thermal stability of each bar serves as a point that is connected to other mean temperatures. Although the basic anhydrous framework structures are constant within each group it must be recognized that the accuracy of the data obtained on stability temperatures is subject to numerous variables, including differences in the interlayer cations present, degree of weathering, purity of the mineral analyzed, particle size, operator variation, instrumental variation, and others. Assignment of Al : Si ratios likewise can be only approximate, but it is guided by ideal mineral compositions, by ideal mean values, or more fortunately in the case of biotite, by a mean value from a specialized report on the mineral (Foster, 1960). Although all the data can be only approximate, the trends shown in the graph are found to be sufficiently consistent that they are considered to be significant.

By moving downward along the line in the dioctahedral, Al-dominant group it is seen that the mean temperatures of maximum stability decrease from about 960°C in muscovite through about 895°C for illite, 860°C for

montmorillonite, to about 775°C for pyrophyllite. In parallel sequence, the Al : Si ratio in the tetrahedral layers change from about 1 : 3 to 0 : 4.

In the Fe^{+++} rich, dominantly dioctahedral pair, glauconite is characterized by a higher Al : Si ratio than is nontronite, and is stable to a higher temperature.

In the trioctahedral group, in which Mg dominates the octahedral layer, the decreasing mean maximum temperature of thermal stability declines with corresponding decrease in tetrahedral Al, except that the behavior of talc is anomalous. No clear cut reason is evident why talc has a relatively high thermal stability in the series. It is suggested that the members of the trioctahedral group possess higher thermal stability than their dioctahedral counterparts, but the differences in composition between the two groups bring in other complexing effects which are difficult to assess, and make a valid comparison open to question.

Differences in Type of Bonding

Coincident with the differences in Al : Si ratio goes a variation in the ionic-covalent bonding in the minerals, which is most likely the basic cause for the differences in their thermal properties. Based on electronegativity computations the Al–O bond is more ionic than the Si–O bond, and the Mg–O bond is more ionic than the Al–O bond. Electronegativity differences between those cations and oxygen are respectively: between Si and O, 1.7; Al and O, 2.0; and Mg and O, 2.3 (Jonas, 1961).

Therefore, the minerals higher in Al : Si ratio, and those containing the more numerous divalent than trivalent elements in octahedral coordination are more ionic in bond character than the others. Moreover, the more highly substituted (by lower-valent ions) phyllosilicate structures require additional interlayer cations to balance charge deficiencies, and these interlayer cations tend to be high in ionic bonding thereby adding significantly to the ionic character of the mineral. Probably this effect accounts for the much higher ionic properties of biotite and muscovite than pyrophyllite and talc.

The effects of ionic, or alternatively covalent, bonding on the thermal and alteration properties of the phyllosilicates may be anticipated from the effects generally attributed to bond types, as have been summarized in Table 2.

By cross-reference to Fig. 1 (also Table 1) and Table 2, between minerals and bond effects, it is seen that through-going consistency occurs between relatively high thermal stability in the minerals, high substitution of Al for Si and Mg for Al, and high ionic bond type.

With respect to alteration by water ("solvent-related" in Table 2) biotite is more readily dissolved in water than is muscovite (Keller, Balgord, and Reesman, 1963). Not uncommonly muscovite alters to illite, and biotite to glauconite. Illite is degraded to expanding illite, or

TABLE 2.—SOME CHARACTERISTICS, AND RELATED EFFECTS, OF IONIC AND COVALENT
BONDS IN COMPOUNDS

Bond Type

	Ionic	Covalent
Temperature related	Long range bond. Interacts by inverse square function. Tolerates vigorous vibrational forces. Therefore, relatively stable at high temperature.	Short range bond. Depends on effective orbital overlap. Does not tolerate vibrational forces as readily as ionic bond of somewhat weaker strength. Stability deteriorates at higher temperatures.
Solvent (as polar, H_2O) related	Bonds weakened by shielding effect of substances having high dielectric constants. Polar solvent molecules attract ions. Therefore relatively unstable in polar solvents.	Bonds scarcely affected by substances having high dielectric constants. No, or little coulombic attraction between atoms and polar solvent molecules. Relatively stable in polar solvents.

"montmorillonite". Jonas (1961) explains the transition from illite to montmorillonite in terms of removal of the more ionic bonded (the more soluble) elements accompanying decrease in particle size as in weathering. Montmorillonite is leached, not to pyrophyllite as in the sequence, but to kaolinite (no substitution of Al for Si) and silica (which is about half covalent bonded). Pyrophyllite commonly occurs as a product of hydrothermal processes operating at a lower temperature than if sericitization had occurred—thus it is consistent in location below muscovite, as shown in Fig. 1.

Other Examples of Ionic-Covalent Bonding Effects

The principle relating high ionic-bond characteristics to high thermal stability is applicable to silicate structures other than three-layer phyllosilicates, provided the comparisons are restricted to isostructural groups, a single reaction series, or minerals very closely associated, wherein the differences are basically in the character of the bonding.

In the plagioclase group, anorthite with 2 Al, 2 Si, and 8 O exhibits higher thermal stability than does albite with 1 Al, 3 Si, and 8 O. Although the Na–O bond is slightly more ionic than is the Ca–O bond, this effect is overshadowed by the greater ionic effect of the second Al–O substituting for Si–O contrasted to albite.

The ratio of Si–O bonds to the more ionic metal cation bonds is smaller in nesosilicates than in inosilicates. Thus, a nesosilicate mineral is more

ionic in character than its inosilicate counterpart. Several mineral representatives of the two structures, but having common ions, are available. Forsterite, Mg_2SiO_4, melts at about 1890°C, whereas enstatite, $MgSiO_3$, melts at about 1540°C. Larnite, Ca_2SiO_4, melts at about 2130°C, and is relatively soluble in water, whereas wollastonite, $CaSiO_3$, melts at about 1540°C, and is relatively insoluble in water. Similar parallel effects occur between the Ba, Sr, Li, Fe, Mn and Na neso- and inosilicate compounds. Others are being investigated.

Within the olivine reaction series, forsterite which is more ionic in character than fayalite, Fe_2SiO_4, melts at about 600°C higher than fayalite.

Between kaolinite and serpentine, serpentine has higher thermal stability, and correspondingly contains more cations with higher electronegativity with respect to oxygen (Mg–O) than does kaolinite (Al–O).

The principle that the character of bonding affects significantly the properties of silicate minerals, including the clay minerals, is extensively applicable.

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