INFLUENCE OF 10Å/14 Å INTERLAYERING ON THE LAYER CHARGE OF GLAUCONITES

ALENA CIMBÁLNÍKOVÁ, *Geological Institute of the Czechoslovak Academy of Sciences, Prague*

ABSTRACT

The relationship of the layer charges (total, octahedral and tetrahedral) of glauconites to the increasing percentage of the expandable layers has been studied on 20 samples of glauconites from the Cretaceous of Bohemia.

The octahedral charge is higher in the composite-layer (total) charge of glauconites, whereas the tetrahedral is always markedly lower. This fact, according with Foster's (1960) view, confirms the position of glauconites in the series of dioctahedral potash micas, the so-called "trisilicic-tetrasilicic series."

With a rising percentage of the expandable component, the total charge of glauconites decreases.

A quadratic dependence has been established between the layer charges of glauconites (total, octahedral and tetrahedral) and the amount of expandable layers. For a pure (10 Å) glauconite, a total charge of 0.92, an octahedral charge of 0.63, and a tetrahedral charge of 0.29 have been inferred by extrapolation.

INTRODUCTION

In dioctahedral phyllosilicates, the layer charge is conditioned by the substitution of the cations of higher valencies in the tetrahedral or octahedral layers by those of lower valencies. Accordingly, the octahedral or tetrahedral layers are carriers of the predominant part of the charge. The total charge is different in the individual groups of phyllosilicates; the highest is that occuring in the group of brittle micas (~ 2), the lowest in the kaolinite-serpentine group (~ 0). In the group of true micas the total charge approaches 1.

Foster (1960) has inferred that the charge center gradually passes from the tetrahedral layers (muscovite) to the octahedral ones (celadonite) in the individual dioctahedral micas, the composite-layer (total) charge being practically the same; in true micas it is near 1; in "illites" it is somewhat lower (0.70–0.95) (Foster, 1954). In this way a continuous series muscovite-celadonite arises [Foster's (1960) concept of a "trisilicic-tetrasilicic series"] in which Al dominates the octahedral positions in muscovite, and Fe in celadonite.

Theoretically-pure (10 Å) glauconite is a member of this muscovite-celadonite series, approaching its celadonite end (Figure 1). As in celadonite, a high degree of substitution in the octahedral layers is typical; however, in pure glauconite unlike celadonite, substitution also occurs in the tetrahedral layers. Natural glauconites (glauconite pellets: Burst, 1958), however, are structurally heterogeneous, being formed by inter-
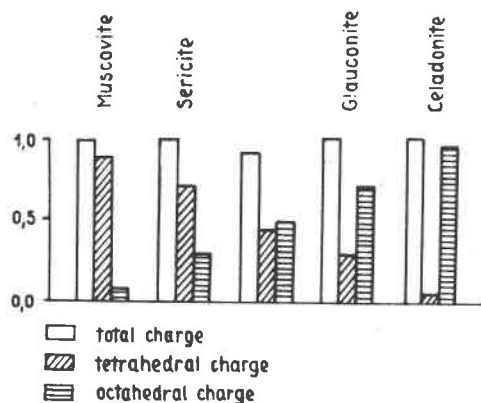
Fig. 1. Histograms showing the total, tetrahedral and octahedral charges of the individual members of a "trisilicic-tetrasilicic series"—according to Foster (1960).

layering of 10 Å (mica) layers and 14 Å (montmorillonite) layers; compare Hower (1961), Manghnani and Hower (1964), Bentor and Kastner (1965), and Cimbálníková (1970).

In montmorillonites (Figure 2), subtitution also prevails in the octahedral layers, it is, however, always less intensive than in glauconites; in the tetrahedral layers it is insignificant, in ideal montmorillonite it would be zero. Hence the total charge of "pure" (10 Å) glauconites and montrillonites is markedly different. Foster (1954) concludes that the highest limit of the total charge in montmorillonites is considerably lower than the lowest limit of this charge in illites.

From the aforesaid, it follows that in natural 10 Å/14 Å glauconites the total charge is determined by two components, the mica and the montmorillonite which markedly differ in their charges.
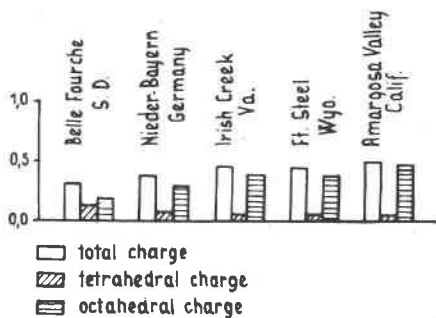

Fig. 2. Histograms showing the total, tetrahedral and octahedral charges of montmorillonites—adjusted according to Foster (1954).

Bentor and Kastner (1965)–whose opinion is so far isolated–maintain that the charge of octahedral layers is often much lower (0.07–0.51) than that of tetrahedral layers (0.41–0.68) in glauconites.

The aim of the present paper is to identify in 20 glauconite samples from the Bohemian Upper Cretaceous the magnitude and the distribution of the layer charge; thus to revise Bentor and Kastner's assertion; and, in addition, to investigate the dependence of the expandable component in glauconites on their layer charge (total, octahedral and tetrahedral). In glauconites this relationship has not yet been studied in detail. Manghnani and Hower (1964) discussing the dependence between the percentage of expandable layers and the potassium content in glauconites, however, assume that this relationship is not a simple linear function.

The X-ray diffraction determinations and the chemical analysis of separated samples of glauconites as described in the accompanying paper (Cimbálníková, 1971a) are the major source of analytical data.

RESULTS AND DISCUSSION

Figure 3 shows the relationship between the established percentage of the expandable (14 Å) layers and the layer charges of glauconites (total, octahedral and tetrahedral) see Cimbálníková, 1971a, Table 2. The figure has been supplemented by fitted curves (quadratic parabolas)
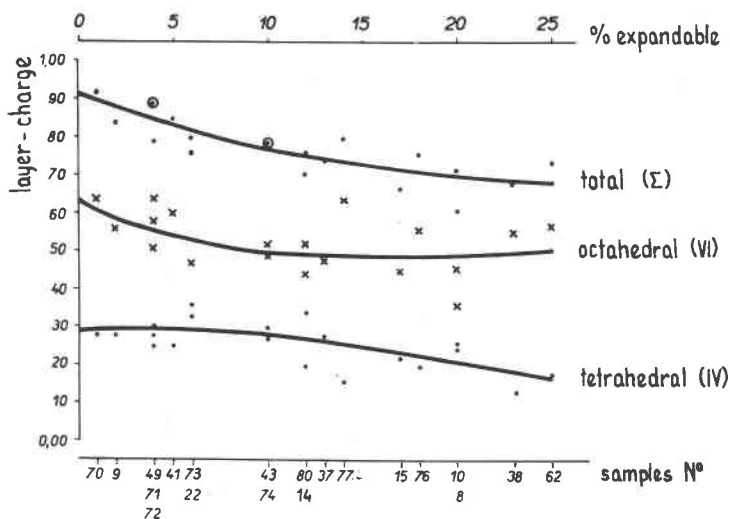

FIG. 3. Relation between the percentage of expandable component and the layer charges of glauconites.

computed by the least squares method. From the figure the following conclusions can be drawn:
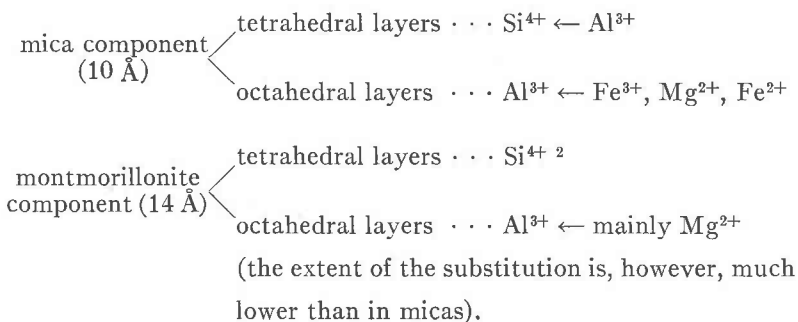
1. In glauconites the octahedral charge is always substantially higher than the tetrahedral one. This statement is in agreement with Foster's (1954) concept of a successive, gradual shift of the charge center in dioctahedral potash micas. On the other hand, it does not agree with Bentor and Kastner's opinion of the predominance of the tetrahedral charge in glauconites.

2. From the course of the individual fitted curves the magnitude of the total charge (0.92), the octahedral charge (0.63), and the tetrahedral charge (0.29) for "pure" (10 Å) glauconites can be inferred by extrapolation. The total charge of glauconite is, therefore, lower than the theoretically assumed charge of true micas ($\sim$1).[1]

3. There exists a quadratic dependence between the layer charges and the expandable component percentage of glauconites; its form, however, is different for each of the partial charges: its curve is concave for the octahedral charge and convex for the tetrahedral.

4. The total charge (*i.e.* the sum of the tetrahedral and octahedral charges) also shows a moderately quadratic dependence.

The opposite form of the fitted curves (quadratic parabolas VI and IV in Figure 3) can also be explained by taking into consideration the kind and extent of isomorphic substitution in tetrahedral and octahedral layers of both interstratifying components in glauconites:

mica component (10 Å)
- tetrahedral layers $\cdots$ $Si^{4+} \leftarrow Al^{3+}$
- octahedral layers $\cdots$ $Al^{3+} \leftarrow Fe^{3+}, Mg^{2+}, Fe^{2+}$

montmorillonite component (14 Å)
- tetrahedral layers $\cdots$ Si^{4+} [2]
- octahedral layers $\cdots$ $Al^{3+} \leftarrow$ mainly Mg^{2+}

(the extent of the substitution is, however, much lower than in micas).

From this scheme it follows that in glauconites which show interlayered (10 Å/14 Å) structures

(a) The tetrahedral charge is directly determined by the 10 Å component only, so that it will diminish with the decrease of this component.

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[1] This fact may be due to a higher number of hydroxyl groups $(OH)^-$ in the structural formula of micas than the theoretically assumed number 2 (Cimbálníková, 1971b).

[2] For simplification's sake, a possible (however, quite negligible) substitution has been omitted.

Hence the convex shape of the fitted curve (parabola IV) in Figure 3. The montmorillonite content affects the tetrahedral charge *indirectly* only by influencing the amount of the 10 Å component in the 10 Å/14 Å ratio;

(b) the octahedral charge is determined directly by the 10 Å component as well as by the 14 Å one; if the same volume of both components is assumed, the 10 Å component represents a much higher charge due to a higher grade of isomorphic substitution in mica minerals. The octahedral charge of glauconites, therefore, will diminish with the decrease of the 10 Å component, but, at the same time, it will gradually increase with the rising percentage of the montmorillonite component. Hence the concave shape of the fitted curve (VI) in Figure 3.

CONCLUSIONS

The layer charges of glauconites (total, octahedral, tetrahedral) do not vary in a simple linear relation to the percentage of the expandable layers but in a quadratic one. The quadratic dependences established can be elucidated most probably by a complicated course of glauconitization which is characterized by continuous chemical-structural variations. These changes, which dependent upon the degree of glauconitization, tend towards the formation of a structure with maximum stability; towards a "pure" 10 Å structure.

Glauconitization can, therefore, be understood, from this point of view, as a progressive transformation of minerals with an interlayered 10 Å/14 Å structure into minerals with a 10 Å structure. Such a transformation does not mean a mechanical exchange of interlayer cations only (as Dietz, 1942; Nagelschmidt and Hicks, 1943 and others assumed ---compare Foster, 1954). It must be associated with more complicated gradual changes in the individual structural positions of both interlayering components such as have been mentioned for 10 Å/14 Å structures by Manghnani and Hower (1964). The complication and gradual character of these changes may be one of the main causes of more complicated, quadratic, dependences (Figure 3). The mechanism of these changes, as far as its relation to the genesis of glauconite is concerned, has been reported in greater detail by Millot, Lucas and Paquet (1966).

REFERENCES

BENTOR, Y. K., AND M. KASTNER (1965) Notes on the mineralogy and origin of glauconite. *J. Sediment. Petrology*, **35**, 155–166.

BURST, J. F. (1958) Mineral heterogeneity in "glauconite" pellets. *Amer. Mineral.* **43**, 481–497.

CIMBÁLNIKOVÁ, A. (1970) Type, extent and mode of interlayering (10Å/14 Å) in glauconites. *Acta Univ. Carol. Geol.*, No. 4, (in press).

———— (1971a) Chemical variability and structural heterogeneity of glauconites. *Amer. Mineral.* **56,** 1383–1390.

———— (1971b) Structural-chemical formulas of glauconites. *Acta Univ. Carol. Geol.,* Supp. 5th Conf. on Clay Mineral. and Petrol., Prague, (in press).

FOSTER, M. D. (1954) The relation between "illite," beidellite and montmorillonite. *Clays Clay Minerals, Proc. Nat. Conf.* **2 (1953),** 386–397.

———— (1960) Layer charge relations in the dioctahedral and trioctahedral micas. *Amer. Mineral.* **45,** 383–398.

HOWER, J. (1961) Some factors concerning the nature and origin of glauconite. *Amer. Mineral.* **46,** 313–334.

MANGHNANI, M. H., AND J. HOWER (1964) Glauconites: Cation exchange capacities and infrared spectra. Part I. The cation exchange capacity of glauconite. *Amer. Mineral.* **49,** 586–598.

MILLOT, G., J. LUCAS, AND H. PAQUET (1966): Evolution géochimique par dégradation et agradation des minéraux argileux dans l'hydrosphéra. *Geol. Rundsch.* **55,** 1–20.