Theses of PhD dissertation

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ANALYTICAL PRACTICE AND CRYSTAL CHEMISTRY OF THE CELADONITE–GLAUCONITE GROUP. THE CRYSTAL CHEMISTRY OF GLAUCONITISATION, BASED ON SOME HUNGARIAN EXAMPLES

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**Introduction**

*Green earth* varieties have been widely used since the Roman times. From the 19th century on, most green earth types have been called *glauconite* or *celadonite*, and the two terms are present in mineralogy and geology also today. Scientific content and relationship of these two terms have been changing continuously and they are mixed up in scientific papers even today.

In the first eight decades of the 20th century they have been distinguished upon *genetic environment*: green grains and earthy masses found in sedimentary environment were called glauconite, whereas those originating from volcanic environment were called celadonite. However, modern nomenclatures (AIPEA, 1980; AIPEA, 1986; IMA, 1998) are clearly based on *crystal chemistry*, although ambiguity is still preserved and reflected in the fact the three nomenclatures apply all the three possible crystal chemical cation position (tetrahedral, octahedral and interlayer, resp.) to differentiate between the two minerals.

The latest nomenclatures (IMA 1998≡AIPEA 2006) agree that celadonite is an iron-rich dioctahedral mica with TOT charge originating predominantly from the octahedral layer, while glauconite is its interlayer-cation-deficient counterpart. Differentiation is thus based on crystal chemistry, but in practice – due to analytical problems arising from small grain size and inhomogeneities, the two minerals are mainly differentiated upon structural characteristics (XPD and FTIR behaviour – according to the 1980 definitions of AIPEA). Up to present, references have not revealed that there are serious discrepancies between the two approaches.

To further complicate the situation, minerals of this group form in certain environments by direct crystallisation, whereas under different conditions (on the sea-bottom, near the sediment-water interface) they appear as a result of a complex crystal chemical evolution. This latter process is known as *glauconitisation*, and the understanding of this process is vital for both oceanology and in palaeoenvironmental reconstructions.

The *crystal chemical relationship* between celadonite and glauconite is currently thought to be similar to the relationship between illite – studied in details due to its significance in hydrocarbon prospecting – and muscovite. *Formation conditions* are significantly different, however: during illitisation, disperse expandable dioctahedral layer silicates of the sediment turn gradually into (interlayer-deficient) mica, as a result of progressing burial: increasing pressure and temperature. Glauconitisation is on the other hand a predominantly chemistry-driven process occurring near the sediment-water interface. In the lack of detailed studies on glauconitisation, the two processes are often made parallel, although we have no proven thermodynamic reason to do that.
Main goals

My work had two basic goals.

The first main goal was to find out the potential and limits of the chemical investigation of the celadonite-glaucnite group by collecting statistical amount of analytical data on a number of well-characterised samples, applying and comparing widely used analytical methods. The quality of chemical data was measured by their crystal chemical applicability, as it has been shown that the modern characterisation of this mineral group is based on crystal chemistry. The basic question was therefore the following: Is it possible to obtain chemical data of high enough quality for crystal chemical calculations on a large number of samples with modern analytical methods? If so, what are the limitations? It was necessary to handle the frequent lack of Fe$^{2+}$-determination and the propagation of the analytical error during formula calculation. Analytical comparability required the highest possible chemical homogeneity of the samples.

The second main goal was the crystal chemical characterisation of the glauconitisation process. A number of models have been proposed in the last 50 years to explain / describe this process. Model proposing researchers tried to reconstruct the stages of glauconitisation through the comparison of recent or fossil samples, which led to camouflaging or rendering uncertain the gist of the process. To avoid this, we were the first to study evolution series represented by fractions obtained through the sequential separation of single samples. This approach eliminates all factors independent of glauconitisation (different starting material, formation conditions and diagenetic history), and the remaining differences between the fractions will directly unveil / reveal the glauconitisation process itself. The studied evolution series originate from Hungarian Cretaceous and Oligocene formations, facilitating the later application of mineralogical results in the Hungarian geological research.

During my work it turned out that the general confusions surrounding the nomenclature of this mineral group even today make it impossible express ideas and results accurately. Therefore it was unavoidable to trace the birth and evolution of the terms glauconite and celadonite, just to be able to handle them on a uniform and unequivocal platform.

The need to show lucidly/ expressively the multivariate process of glauconitisation arose during my work, too. Published graphical representation systems of crystal chemistry were therefore listed and evaluated upon their applicability to iron-rich dioctahedral micas, highlighting their advantages and disadvantages, too. Recognising their disadvantages, we set the goal of designing a new graphical representation system that elucidates the process of glauconitisation.
The applied methods can be divided into several groups.

Beside the routine processing of related current references, outlining the theoretical background required the setting up of a coherent crystal chemical database, uniform in its approach. This database includes earlier published analyses (approximately 600 entries) complemented by crystal chemical calculations. Confusions in the terms rooted in the distant past required the systematic processing of historical original works back to the middle of the 18th century.

Sample selection was the result of field work supported by geologists familiar with the studied formations. To better understand the crystal chemical changes during glauconitisation and the crystal chemistry of the celadonite-glaucophane group, properly separated green layer-silicates of six sedimentary formations were studied in detail. These formations are: Upper Oligocene Eger Formation (sandstone, sample codes: NY1, NY3, EWT), Lower–Middle Cretaceous Sümeg Marl Formation (limestone, sample code: SK), Middle Cretaceous Pénzeskút Marl Formation (limestone, sample code: PM) and the Lower Jurassic Úrkút Manganese Ore Formation (banded manganese carbonate ore).

Each sample was submitted to special separation processes designed by our working group in order to obtain chemical homogeneity required by our goals and not yet achieved by earlier researchers of this field.

Following traditional optical microscopy (stereomicroscope, transmitted light polarizing microscope), appr. 900 grains were selected for detailed morphological study by scanning electron microscopy (SEM). In the next stage, grains were embedded in epoxy resin, and their chemical composition was studied by quantitative local chemical methods (WDX, EDX, LA-ICP-MS).

Main and trace element composition of separated fractions of evolution series were also determined by bulk methods (ICP-AES, ICP-MS). Wherever possible, Fe\(^{2+}\)-content was determined by titration, too.

Comparison of laboratories (Geological Institute of Hungary Budapest and the Natural History Museum, London) and methods (local vs. bulk; WDX vs. EDX) played an important role during designing the measurements. At the local chemical methods (WDX, EDX), the effect of analytical conditions (size of the analysed area, analysis order etc.) on the measured compositions was also tested.

The structural methods X-ray powder diffraction (XPD) and Fourier-transform infrared spectroscopy (FTIR) were mainly applied for phase identification, at some evolution series for the documentation of the structural changes and to check sample purity.
Theses

1. With the help of appr. 1300 new chemical analyses it has been confirmed that all of the applied main element analytical methods – designed in accordance with our approach – are capable of yielding chemical data suitable for crystal chemical calculations in the celadonite-glaucnite group. Systematic differences were recorded, however, between WDX and EDX analyses, local (WDX, EDX) and bulk (ICP-AES) methods and the single ICP-AES laboratories. These results allow the crystal chemical evaluation of our own data, as well as the crystal chemistry related quality assessment of analyses available in the literature (appr. 600 analyses).

2. It has been shown that concerning the $\text{Fe}^{3+}$-Al substitution in the octahedral sheet of dioctahedral layer-silicates the crystal chemical space is continuous at both smectites and interlayer-deficient micas. For smectites, proof is provided by traditional green grain series undergoing glauconitisation, while for interlayer-deficient micas by the atypical green grain series of the Sümeg Marl Formation. These results suggest that the iron-rich ($^{\text{VI}}\text{Al} / \left( ^{\text{VI}}\text{Al} + ^{\text{VI}}\text{Fe}^{3+} \right) < 0.5$) counterpart of montmorillonite should be defined as a new mineral species and that the illite definition of IMA should be extended.

3. The starting material of glauconitisation was found to be montmorillonite, which is different from “traditional” montmorillonites in having K as the dominant cation in the interlayer (and not Na or Ca). The crystal chemical evolution goes through the steps montmorillonite => „$\text{Fe}^{3+}$-montmorillonite” / nontronite => glauconite-GG => glauconite-CG.

4. It has been shown that the octahedral occupancy ($B_0$) > 2.00 is a real feature of glauconitising grains (i.e. green grains evolving in the sediment) and not a consequence of analytical error. $\text{Fe}^{2+}$ content estimation assuming $B_0 = 2.00$ is therefore not a proper formula calculation method at these materials. Giving a rough estimate of the $\text{Fe}^{2+}$ content upon the grain colour seems to be more adequate.

5. From a crystal chemical viewpoint, glauconitisation has been divided into two stages. In the first stage, the amount of $^{\text{IV}}\text{Al}$ increases, and the accompanying decrease of the tetrahedral cation charge facilitates the incorporation of K into the interlayer space (a feature similar to illitisation – relevant samples: Pénzeskút Marl Formation, Fig. 1, whitish grains of the Sümeg Marl Formation). In the second stage of glauconitisation, the decrease of the octahedral cation charge facilitates the incorporation of K into the
interlayer space, and the composition of the tetrahedral layer is not changing significantly (a feature different from illitisation – relevant samples: Eger Formation – NY1 – Fig. 2, NY3, EWT).

6. It was demonstrated that at the beginning of glauconitisation, octahedral occupancy is significantly higher (B$_O$) than the ideal dioctahedral value, and it is not changing much in the first stage of glauconitisation. In the second stage, however, the release of $^{VI}$Al exceeds the incorporation of $^{VI}$Fe$^{3+}$ and $^{VI}$Fe$^{2+}$, thus B$_O$ decreases, approaching ideal dioctahedrality. The decrease of the octahedral cation charge (X$_O$) originates predominantly from the decrease of B$_O$ (“increase of vacancies”, Fig. 3). The composition of the octahedral sheet changes the same way during both stages of glauconitisation: Al content decreases, Fe content increases (in both valence states), while the amount of Mg is relatively stable.

7. A new, combined graphical representation system has been designed that represents the crystal chemistry of the celadonite-glauconite group better than the previous ones. This system consists of the combined application of the 3D charge diagram (axes x, y, z are the octahedral cation charge, X$_O$, the ratio $^{VI}$Al / ($^{VI}$Al + $^{VI}$Fe$^{3+}$) and the interlayer cation charge, X$_{IL}$, resp.; Figs. 1–2) and the octahedral occupancy–octahedral charge (B$_O$–X$_O$) diagram (Fig. 3). The 3D charge diagram is able to show the main discrimination borders of all three nomenclatures and allows the definition of smaller crystal chemical space sections by the combination of nomenclatures. Some nomenclature borders (IMA: $^{VI}$R$^{2+}$ / ($^{VI}$R$^{2+}$ + $^{VI}$R$^{3+}$)) can migrate as a function of octahedral occupancy, but the diagram retains its crystal chemical character in all cases. The crystal chemical space occupied by the celadonite-glauconite group is best dissected by the combination of the AIPEA 1980 and IMA 1998 nomenclature. The introduction of the two-letter suffices allows the unequivocal expression of chemical composition, without the introduction of new terms.

8. LA-ICP-MS has been applied for the first time for the systematic study of the rare earth element (REE) content of the celadonite-glauconite group. It has been shown that the true REE content of these green layer-silicates is significantly lower (by 1–2 orders of magnitude) than previously published values (ICP-MS, INAA). Comparing local (LA-ICP-MS) and bulk (ICP-MS, INAA) analytical data, we managed to explain this phenomenon: higher REE concentrations are caused by the subordinate, intragrain presence of REE-concentrating phases that cannot be removed by separation.
9. The true REE pattern of glauconites is similar in shape to the REE patterns of sedimentary rocks and the upper crust, though the REE concentrations are lower (0.1–0.5 PAAS) already at the beginning of glauconitisation and are further decreasing during the process.

10. Pores and cracks of the high-density (\(\rho > 2.63 \text{ g/cm}^3\)) grains of sample EWT are filled by a yet unknown Ca-REE-phosphate phase, the composition of which can be expressed as (normalised to 4 O) \((\text{Ce}_{0.42}\text{La}_{0.16}\text{Nd}_{0.12})\text{Ca}_{0.36}\text{P}_{1.05}\text{O}_4\). The REE : Ca ratio is approximately 2 : 1.

11. The green grain series of the Sümeg Marl Formation differs in both appearance and composition from the traditional sedimentary green interlayer-deficient micas: the high-density grains may be regarded as the first description of allochtonous granular celadonite-CC. The grains are sometimes pseudomorphs after elongated minerals (with traces of prismatic cleavage), and often preserve signs of alteration.

12. The identification of the illitising(?) gray grain series (up to present without chemical data) in the non-magnetic fractions of the Sümeg Marl Formation revealed that not only iron-rich dioctahedral layer silicates (glauconites evolving in sediments) may form aggregates by orders of magnitude larger than the size of clay minerals. It is an important methodological conclusion that during the clay mineralogical study of sedimentary rocks it is necessary to conduct \(\mu\)m range textural studies beside the conventional preparation (crushing, carbonate dissolution etc.) of the clay fraction.

**Conclusions**

With the acquisition and evaluation of appr. 1300 new main element analyses, obtained under controlled and comparable conditions, complementing the appr. 600 analyses published so far on the celadonite-glauconite group, we managed to set up the requirements of obtaining high-quality analytical data (good for crystal chemical calculations) on the celadonite-glauconite group minerals. This gives us the chance to identify the minerals of this group – in agreement with both IMA and AIPEA recommendations – upon chemical data, obtained even by local chemical methods (EPMA, SEM+EDX), allowing the study of a high number of samples within reasonable time and cost limits.

In agreement with our preliminary assumptions, the multi-step separation technique (involving separation upon grain size, magnetic susceptibility and density) designed by our working group separates glauconitic grains of a given population according to maturity (interlayer cation content
etc.). Fractions obtained by the labour-intensive separation represent evolution series, offering the only opportunity to the direct study of glauconitisation.

With a statistical number of analyses, obtained on the evolution series of five Hungarian glauconite-bearing samples, we managed to reconstruct convincingly the crystal chemical changes (reflected in changing chemical composition) occurring during glauconitisation.

Having documented the true REE content of the celadonite-glauconite group and revealed the REE pattern distorting effect of syn- or postdiagenetic REE-concentrating accessory minerals we can avoid the inadequate geochemical application of this mineral group in the future.

Publications related to the subject of the PhD dissertation

Papers

International conference abstracts
Conference (Wien), Mitteilungen der Österreichischen Mineralogischen Gesellschaft, 146, 288–289.


Fig. 1. The first stage of glauconitisation, demonstrated by the green grain series of the Pénzeskút Marl Formation, on two sections of the 3D charge diagram. The direction of evolution (increasing aggregate density) is shown by an arrow. Analyses clearly get diverge from the red diagonal (Si = 4), reflecting increase of $^{VI}$Al. Chemical evolution of the grains: montmorillonite $\Rightarrow$ „Fe$^{3+}$“-montmorillonite $\Rightarrow$ glauconite-GG.

![Diagram showing $^{VI}$Al / ($^{VI}$Al+$^{VI}$Fe$^{3+}$) vs. Oktaéderes kATIONLÖTÉS ($X_0$)](image)

Fig. 2. The second stage of glauconitisation, demonstrated by the green grain series of sample NY1, Eger Formation, on two sections of the 3D charge diagram. The direction of evolution (increasing aggregate density) is shown by an arrow. Analyses plot parallel to the red diagonal (Si = 4), indicating that the evolution is „isotetrahedral“. Chemical evolution of the grains: nontronite $\Rightarrow$ glauconite-GG $\Rightarrow$ celadonite-CG.

![Diagram showing $^{VI}$Al / ($^{VI}$Al+$^{VI}$Fe$^{3+}$) vs. Oktaéderes kATIONLÖTÉS ($X_0$)](image)

Fig. 3. The second stage of glauconitisation, demonstrated by the green grain series of sample NY1, Eger Formation, on the $B_0$–$X_0$ diagram. The direction of evolution (increasing aggregate density) is shown by an arrow. For the decrease of the octahedral charge ($X_0$) the release of $^{VI}$Al, and later the $^{VI}$Al $\Rightarrow$ $^{VI}$Fe$^{2+}$ substitution is responsible.

![Diagram showing $^{VI}$Al vs. Oktaéderes betÖLTÖTTSég ($B_0$)](image)