CRITICAL EVALUATION OF THE ANALYTICAL DATA ON DIOCTAHEDRAL IRON-RICH MICAS AND RELATED MINERAL PHASES PUBLISHED IN THE LITERATURE

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From many respects, it is hard to obtain high-quality chemical data of iron-rich dioctahedral micas (the true mica celadonite and the interlayer-deficient mica glauconite) and the related phases (*e.g.* "Fe-illite", "skolite"). Firstly, the sample is often inhomogeneous: the less evolved glauconitic grains regularly contain inclusions of quartz, feldspar, apatite *etc.* and may be stained with iron oxy-hydroxides, while celadonite, primarily a hydrothermal alteration product of basalt, often forms only thin encrustations and is readily mixed with other clay minerals or zeolites. This high grade of inhomogeneity could still be avoided by the application of electron probe microanalysis, however, these minerals contain a considerable amount of iron in both valence states, and for the determination of the Fe^{3+} / Fe^{2+} ratio either Mössbauer spectroscopy or wet chemistry is needed.

Studying the crystal chemical space occupied by these minerals, we set up a database including all the full chemical data accessible in the earth science literature. At the moment, the database contains more than 630 records, allowing us to draw some conclusions on the quality of these data.

We found that many authors neglect publishing the measured data (oxide wt %) and give only the calculated formula (atomic coefficients). These formulae often prove erroneous from a crystal chemical point of view, and, without the original data, it is impossible to trace back where the mistake was made. Several tens of analyses were discredited (suspecting either mixed material or analytical error) on structural constraints like Si > 4.0 *apfu* (formula calculated for 11 O), octahedral occupancy > 2.5 (official limit for dioctahedral layer silicates), interlayer occupancy > 1.0 *etc*.

Only half of the remaining data, approx. 300 analyses, contained measured FeO–Fe_2O_3 values with the proportion of Fe^{2+} being in the range 0–40%. For those analyses lacking these values, the authors adopted one of the following processes: they considered the total amount of iron as Fe^{3+}, or they calculated the formula for perfect dioctahedrality (*i.e.* octahedral occupancy = 2.00), even in such nomenclature-inspiring papers like LI *et al.* (1997). From these 300 "complete" analyses we found that the octahedral occupancy has an approximately normal distribution, with the maximum near 1.99–2.01 for phases containing K = 0.85–1.00 *apfu* and 2.01–2.03 for K = 0.6–0.85 *apfu* (values are in the range 1.95–2.10). We expect that in our data set the less evolved – pale green, more smectite-like – grains are underrepresented.

For showing the effect of the occupancy *vs*. iron valence state calculations, as an example, a well-known celadonite (E' of BUCKLEY *et al.*, 1978) with given FeO–Fe_2O_3 concentrations was selected. With increasing octahedral occupancy (oct. occ.), the interlayer charge remained relatively constant, however, the amount of divalent iron increased dramatically: from 6% (oct. occ. = 1.95) to 46% (oct. occ. = 2.05). More important, the nomenclature-related (RIEDER *et al.*, 1998) discriminant value $^{VI}Al / (^{VI}Al + ^{VI}Fe^{3+})$ changed from 0.32 to 0.51, crossing the border between Fe-rich and Al-rich members. Inversely, if the amount of Fe^{2+} is estimated to be higher, the octahedral occupancy increases. It comes from two facts: (1) due to the lower amount of oxygens (each Fe^{3+} is accompanied by 1.5 O, while each Fe^{2+} by only 1 O), a higher normalisation factor is needed for the 11 O-based formula, thus the amount of each component increases; (2) as the amount of Si increases, it forces part of the tetrahedral Al into the octahedral layer. The relationship between the amount of Fe^{2+} and the octahedral occupancy is linear.

Plotting the formulae into the IMA nomenclature diagram (RIEDER *et al.*, 1998), we found that several, from a crystal chemical point of view acceptable, formulae plot outside the diagonal border of the celadonite and glauconite boxes due to imperfect (≠ 2.00) dioctahedrality. From this respect, plotting into the IMA diagram should be handled with care.

References

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