TI AND AL SUBSTITUTIONS IN PHLOGOPITES FROM THE SUWALKI MASSIF-TYPE ANORTHOSITE, NE POLAND

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Intercumulus titanium-phlogopites occur in leuco- and gabbro-noritic cumulates from the Suwalki anorthosite massif, NE Poland. The degree of Ti-enrichment in the micas is variable and ranges from 2.59 to 9.48 wt.%. The variation of composition also concerns FeO (6.85-19.63 wt.%), MgO (9.79- 20.09 wt.%), with a Mg/(Fe+Mg) ratio ranging from 0.471 to 0.839, Al₂O₃ (13.17-16.75 wt.%) and K₂O (7.88-10.78 wt.%).

Substitution mechanisms for Ti and octahedral Al have been determined and suggest the presence of exchange vectors involving octahedral and tetrahedral cations. In samples characterized by the lower Ti-content (Ti: 0.144-0.213 *p.f.u*), the Ti-incorporation mechanism is: ${}^{[6]}\text{Ti}^{4+} + {}^{[6]}\Box = 2({}^{[6]}\text{Mg}^{2+}, {}^{[6]}\text{Fe}^{2+}),$

where [6] corresponds to a vacancy in octahedral coordination. In the two groups with intermediate (Ti: 0.160-0.367 p.f.u) and high Ti-content (Ti: 0.489-0.557 p.f.u)., the Ti-substitution mechanism is different from the first group and can be represented by the substitution mechanism:

 $^{[6]}\text{Ti}^{4+} + 2^{[4]}\text{Al}^{3+} = (^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+}) + 2^{[4]}\text{Si}^{4+}.$

A variation of the octahedral aluminium content is only present in the two groups with the lower and intermediate Ti-content. This cation is incorporated in the phlogopite structure by the following substitution mechanism:

 $(^{[6]}Mg^{2^+} + {^{[6]}Fe^{2^+}}) + {^{[4]}Si^{4^+}} = {^{[6]}Al^{3^+}} + {^{[4]}Al^{3^+}}$. In the group with the higher Ti-content, the absence of [6]Al3+-substitution is related to the high K content of the samples. Indeed, this substitution is responsible for a contraction of the interlayer crystallographic site and is thus very limited in highly potassic micas.

In the twenty past years, several authors have proposed that deprotonation can be the most important Ti-substitution mechanism in high grade metamorphic and magmatic phlogopites. Deprotonation mechanism can be represented by the following reaction:

 $(Mg, Fe)^{2+} + 2OH^{-} = Ti^{4+} + 2O^{2-+}$. In order to verify the importance of deprotonation in the phlogopites from Suwalki, an infrared spectroscopic study was carried out on the micas. The relative area of the Mg₃-OH absorption band is compared with the Ti-content for 8 samples. The lack of correlation between the two parameters permits us to consider the total absence of deprotonation in phlogopites from Suwalki.