

SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBIQUITOUS MINERALS AND MATERIALS

Ordering kinetics in synthetic $\text{Mg}(\text{Al},\text{Fe}^{3+})_2\text{O}_4$ spinels: Quantitative elucidation of the whole Al-Mg-Fe partitioning, rate constants, activation energies†

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ABSTRACT

In this study, we report results of the application of a novel procedure for modeling cation ordering in two synthetic $\text{Mg}(\text{Al}_{2-y}\text{Fe}_y^{3+})\text{O}_4$ spinels ($y \sim 0.39$ and 0.54 , samples F39 and F54, respectively). The kinetic profiles suggest a two-stage mechanism, with rapid intersite exchange of Fe^{3+} with Mg followed by slow exchange of Al with Mg. The trial to apply classical approaches, based on explicit solutions of the differential equations corresponding to single-cation (Sha-Chappel model) or two-cation (Müller model) exchange reactions, proved not feasible in the whole time range, thus implying a lack of information about exchange processes involving the Fe^{3+} cation. Therefore we decided to adopt an alternative methodology where a multistep pathway is simulated by Gepasi modeling. The suggested set of reactions and the simultaneous solving of the related rate laws allowed us to calculate rate constants and corresponding activation energies not only for the Al/Mg cationic interchange (257 and 264 kJ/mol for the F39 and F54 samples, respectively), but also, for the first time in such kind of samples (three cations with two sites), for the Fe/Mg cationic interchange (204 and 234 kJ/mol for low- and high- Fe^{3+} samples, respectively).

The evaluation of the significant effect of the iron content, which actually inhibits Mg-Al exchange between the T and M sites, provided new insights useful for the construction of geothermometers based upon iron-bearing spinels.

Keywords: Intersite cation exchange, spinels, kinetics, rate constant, activation energy, geothermometers