

Questioning magnetite key role on H₂ generation yields during alteration of Fe-rich rocks

UGO GEYMOND^{1,2}, OLIVIER SISSMANN¹, ISABELLE MARTINEZ³ AND LAURENT TRUCHE⁴

¹IFP Energies Nouvelles

²IPGP CNRS UMR7154

³Institut de Physique du Globe de Paris

⁴ISTerre, University Grenoble Alpes

Presenting Author: geymond@ipgp.fr

Fe-spinel corresponds to a solid-solution between pure magnetite ($\text{Fe}^{\text{III}}_{1.00}[\text{Fe}^{\text{II}}_{1.00}, \text{Fe}^{\text{III}}_{1.00}]\text{O}_4$) and pure maghemite ($\text{Fe}^{\text{III}}_{1.00}[\text{Fe}^{\text{II}}_{0.00}, \text{Fe}^{\text{III}}_{1.67}, \square_{0.33}]\text{O}_4$, where $()$ and $[\]$ refers to the tetrahedral and octahedral sites, respectively. The symbol \square stands for vacancies and occurs specifically in octahedral cation positions of the mineral lattice to ensure the overall neutrality of the mineral [1]. The stability of one endmember with respect to the other, which determines the $\text{Fe}^{\text{II}}/\text{Fe}_{\text{tot}}$ ratio in the mineral, was found to highly depend on pH-Eh conditions [2].

Fe-spinel is known to form during alteration of Fe-bearing minerals associated with H₂ generation such as Fe-carbonate or Fe-silicate [3,4,5]. It is usually assumed that pure magnetite is formed during such reaction since conventional characterization tools such as XRD cannot quantify properly the ratio of pure maghemite and pure magnetite within Fe-spinel.

Among all the tools designed to study Fe contained in a given solid sample, ⁵⁷Fe Mössbauer spectroscopy is probably one of the more efficient as it allows to determine both Fe speciation and its distribution between tetrahedral and octahedral sites, with an uncertainty below 1 at% [6]. Up to now, it has been only little used in the research field of natural H₂.

Based on some practical examples from experimental work, we present here to what extent the variability in Fe-spinel composition can affect yields of H₂ generation estimated from mass balance calculation with Fe oxidation. From this, we recommend the use of ⁵⁷Fe Mössbauer spectroscopy as a fundamental tool to properly constrain H₂ generation yields from the alteration reactions investigated.

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