

Chemical signatures in magnetites

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Magnetite is an iron oxide common on Earth formed both inorganically and biogenically. Inorganic magnetite can be produced both as a primary and as a secondary phase following decomposition of a precursor phase (Jimenez-Lopez et al., 2009). As a primary phase, magnetite is produced from aqueous solutions containing Fe^{3+} and Fe^{2+} . The thermal decomposition of ankerites under a CO_2 -rich atmosphere is the most studied method for obtaining magnetite as a secondary phase. Biogenically, magnetite can be formed through both biologically-induced mineralization (BIM) and biologically-controlled mineralization (BCM). Foreign cation incorporation in magnetites is a topic of growing interest, mainly because of their applications in nanotechnology and because of the use of those magnetites to recognize bacterial activity, in both terrestrial and extraterrestrial sediments and rocks (Thomas-Keprta et al., 2000). On one hand, the incorporation of cations other than iron into the structure of nanomagnetites seems to alter the magnetic properties of these nanoparticles and thereby expanding the range of application of these nanoparticles (Prozorov et al., in preparation). On the other, the chemical purity of nanomagnetites is one of the criteria integrating the Magnetite Assay for Biogenicity package (proposed by Thomas-Keprta et al. (2000) to distinguish biologically produced magnetites.

In this study, the incorporation of calcium, magnesium and manganese into the crystalline structure of inorganic magnetites, obtained as a primary and secondary phase (the latter from Jimenez-Lopez et al., 2012), and BIM magnetite produced by *Shewanella oneidensis* is studied. The results were compared with BCM magnetite produced by *Magnetospirillum gryphiswaldense* (Prozorov et al. in preparation). In our study, only manganese was incorporated into the crystal structure of biogenic (both BCM and BIM) and inorganic magnetites, while Mg^{2+} was only incorporated in inorganic magnetites (both primary and secondary). However, Ca^{2+} was not incorporated into the crystal structure of either primary inorganic and biogenic magnetites, but was incorporated into secondarily produced magnetites formed via the thermal decomposition of ankerites. Both the relative dissimilarities in the ionic radii and the type of process by which magnetite forms are responsible for the differences in the incorporation of the foreign cations. While Mn^{2+} has an ionic radius similar to that of Fe^{2+} (0.66 Å vs 0.63 Å, respectively), Mg^{2+} is smaller (0.57 Å) and Ca^{2+} is much larger (1 Å). Moreover, when magnetite forms via the topotactic decomposition of a precursor which already had foreign cation substitutions, the resulting magnetite bears a chemical fingerprint of the precursor, allowing for the incorporation of cations with ionic radii very different to that of Fe^{2+} . Therefore, the presence of foreign cations in natural magnetites may be useful in distinguishing how those magnetites were formed.

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