Determination of cation site occupancies in natural magnetite by X-ray absorption spectroscopy and X-ray magnetic circular dichroism

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Magnetite ($Fe^{3+}{}_2Fe^{2+}O_4$) is the most abundant member of the spinel group of minerals. It is present throughout the Earth's crust and uppermost mantle and is the main contributor to rock magnetism. Fe^{2+} and Fe^{3+} in natural magnetite can be replaced by other metallic cations, often with the same charge and similar ionic radius, to form substitutional series. I will present the investigation of cation distributions in natural ferrite spinels, some containing large amounts of Mg, Ti, Mn and Zn, using the element-, site-, and symmetry-selective spectroscopic techniques of L2,3 X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD). A number of XMCD studies have been carried out on synthetic stoichiometric and non-stoichiometric magnetites. These studies, involving non-bulk materials such as thin films, nano-particles and multilayers, draw attention to the versatility and value of the XMCD technique. However, a systematic XMCD study of natural bulk magnetite has not previously been carried out and, in this presentation, the value of this technique for determining site occupancies, cation distribution and the effects of non-stoichiometry in these chemically complex, naturally occurring magnetic materials is demonstrated.