Ferroan geikielite and coupled spinel-rutile exsolution from titanohematite: Interface characterization and magnetic properties

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ABSTRACT

Extensive negative aeromagnetic anomalies in the Modum area, south Norway, derive from rocks containing ilmenite with hematite exsolution, or hematite with ilmenite exsolution, carrying strong/stable reversed remanence. Here we describe a 2.5 cm thick high-temperature metamorphic vein of exsolved titanohematite. Reflected-light and EMP analyses show it contains three types of exsolution: spinel plates on (001); rutile blade satellites on spinel oriented at angles of ~60–90° to titanohematite (001); and lamellae 0.1–0.3 μm thick too fine for EMP analyses, also parallel to (001). Powder XRD gave a = 5.0393 Å, c = 13.7687 Å, V = 302.81 Å^3 for titanohematite (≈Ilm9), and unrefined reflections of rutile and geikielite. Overlap EMP analyses showed enrichment in MgO, TiO_2, and lack of Al_2O_3, indicating a mixture of titanohematite and geikielite. Non-overlap analyses showed the titanohematite is 6%$Fe^{2+}TiO_3$, 2%$MgTiO_3$, 92% Fe_2O_3, generally confirmed by TEM-EDX analyses that also showed the geikielite is 30%$Fe^{2+}TiO_3$, 70%$MgTiO_3$.

Orientation and interface relationships between exsolutions and host titanohematite were characterized with TEM, using conventional and high-resolution imaging complemented by selected-area electron diffraction. Spinel shares (111) with (001) of titanohematite and geikielite (001) the same. The epitactic relationship between rutile and titanohematite, previously not well constrained, was estimated from reflected-light and TEM images and lattice-fit studies. The $\boldsymbol{a}_1$ axis of rutile is parallel to $\boldsymbol{a}_1$ of hematite and $\boldsymbol{c}$ of rutile is normal to $\boldsymbol{a}_2$ of hematite, all in the hematite basal plane, which, however is not a phase interface. The rutile appears to occur in blades within prism planes in titanohematite located ~69° from $\boldsymbol{a}$ axes of hematite, with long axes of the blades oriented in a minimum strain direction within the planes at ~63° from the (001) basal plane.

Spinel and rutile, analyzed by EMP, exsolved first. Spinel gave 96%$MgAl_2O_4$, 3%$FeFe_2O_4$, Mg/total R^{2+} = 0.98. Magnesian/aluminous spinel lacking Ti exsolved from titanohematite in coupled exsolution with ferrian rutile, where combined components were dissolved as corundum/geikielite components in high-T aluminous magnesian titanohematite. Early exsolution lowered geikielite, and eliminated the corundum component. Later fine exsolution of ferroan geikielite moved the titanohematite closer to Fe_2O_3.

Mg^{2+} has no magnetic moment, but breaks up linkages between Fe atoms, lowers Néel Ts, and produces unusual low-T properties. This titanohematite has Néel T, 873 K (600 °C). Geikielite at 70%$MgTiO_3$, is far beyond its theoretical nearest-neighbor percolation threshold at 30.3%$MgTiO_3$. However, the sample shows a negative magnetic exchange bias below 25 K and low-T remanence lost above ~40 K. Such properties are reported in samples containing thin ilmenite lamellae in titanohematite, in theory with odd numbers of Fe layers, where exchange bias is linked to lamellar magnetism at the phase interfaces, when the ilmenite becomes a high-anisotropy magnet in a magnetically softer host. Potential explanations for the behavior of ferroan geikileite are discussed.

Keywords: Electron microscopy, geikielite, spinel, rutile, titanohematite, metamorphic petrology, phase equilibria, magnetic properties, XRD data