The Mechanism of Exsolution of Hematite From Iron-Bearing Rutile

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Abstract. Natural iron-bearing rutile, formed under low temperature hydrothermal conditions, is chemically homogeneous on an electron-microscope scale (at a resolution of about 10 Å). On annealing at temperatures between 475°C and 600°C precipitation of an iron-rich phase occurs. The precipitation sequence involves two transitional stages before the formation of hematite, the equilibrium precipitate. The first phase is coherent with the rutile structure and has the general characteristics of Guinier-Preston zones. The second transitional phase is a monoclinic variant of the rutile structure and is partially coherent with the matrix. Annealing experiments enable a Time-Temperature-Transformation (TTT) plot to be constructed for the exsolution process and the kinetics are interpreted in terms of the structural changes involved at each stage of the process.

Introduction

Rutile, TiO₂, occurs in a wide range of geological environments and appears to form under widely differing temperature conditions. When rutile crystallizes at moderate to low temperatures (below about 450°C) such as in hydrothermal replacement reactions, it typically contains notable amounts of Fe impurities, and the possibility arises that such a solid solution may be metastable at low temperatures with respect to the exsolution of an iron bearing phase. In a study of rutiles from the hydrothermal mineralization at Mt. Perry, Queensland (Putnis and Wilson, 1978) it was shown that while the iron-bearing rutiles were originally homogeneous on an electron microscope scale, experimental annealing at temperatures between 475°C and 595°C resulted in the exsolution of hematite, even in specimens containing as little as 0.5 wt% Fe. The kinetics of this exsolution process were also described and the implications to the geothermometry of such mineralization discussed. In this paper the mechanism of the exsolution of hematite from rutile will be examined, with special reference to the formation of transitional (intermediate) phases.
Phase relations on the join FeO – Fe₂O₃ – TiO₂ have been studied at high temperatures (MacChesney and Muan, 1960; Webster and Bright, 1961) and recently reviewed by Lindsley (1976). Although approximately 3 mol% Fe₂O₃ may be dissolved in rutile at 1400°C, the extent of miscibility at low temperatures is not known. Natural rutiles with around 1% Fe₂O₃ are common. At high temperatures the change in stoichiometry resulting from the substitution of Fe for Ti is accommodated by the development of crystallographic shear planes (Bursill, 1974); no similar observations on natural rutiles have been published; in this paper the behaviour of iron-bearing rutiles at high and low temperatures is contrasted.

Stable equilibria at temperatures below about 600°C on the join TiO₂ – Fe₂O₃ involves the coexistence of rutile and hematite, and in considering the exsolution of hematite from iron-bearing rutile a comparison of the structures of the two end members is necessary.

Rutile has a tetragonal structure \((a = 4.59 \, \text{Å}, \, c = 2.95 \, \text{Å})\), composed of strings of edge-shared TiO₆ octahedra in two mutually perpendicular orientations and joined by corner sharing. It is commonly idealized by a small distortion (rotation of the strings by approximately 12°) which puts the anions into perfect hexagonal closepacking, with the cations occupying alternate rows of octahedral interstices parallel to the \(c\) axis (see e.g. Hyde, 1976). Such a distortion flattens the oxygen layer parallel to the \((100)\) planes in rutile, but exaggerates the puckering on the \((010)\) planes. A rotation in the opposite sense produces the reverse situation. For our purposes we can consider that a small distortion of the structure can result in hexagonal close-packing of the anions parallel to either \((100)\) or \((010)\). Rutile has a two layer repeat…ababab…normal to \((100)\), with the spacing between the layers being 2.29 Å.

In hematite, the anions are very nearly hexagonally closepacked, the close-packed layers forming planes parallel to \((001)\) of the hexagonal cell. The cations occupy two-thirds of the octahedral sites. Hematite has a six layer repeat normal to \((001)\), and the cell dimensions \((a_h = 5.03 \, \text{Å}, \, c_h = 13.74 \, \text{Å})\) indicate a spacing between the layers of 2.29 Å.

Apart from this similarity, the structures of rutile and hematite are quite different in the way that the cations are ordered among the octahedral sites and no appreciable solid solution can exist between them. In considering exsolution in this two-phase system, these similarities and differences must be borne in mind when examining the mechanisms which are likely to operate during the process.

**Experimental**

The rutile used in this study is from specimen P32 from Mt. Perry, Queensland and described by Putnis and Wilson (1978). Electron microprobe analysis of separated grains gave the following composition (in wt%): \(\text{TiO}_2 = 98.66 \ (0.40); \ \text{FeO} = 0.55 \ (0.06); \ \text{V}_2\text{O}_3 = 0.28 \ (0.03)\). The valence state of the Fe could not be determined but later evidence suggests it is mainly \(\text{Fe}^{3+}\). These figures are the average of 12 analyses and the standard deviations are given in parentheses. The analyses were carried out by X-ray energy dispersive analysis using an