

SHORT COMMUNICATIONS

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The chemical state of Fe in rutile from an albitite in Norway

THE substitution of Ti by Fe in natural rutiles has been studied in only a relatively limited number of papers. Deer *et al.* (1962) listed analyses of six natural rutiles with molar Fe/(Ti + Fe) ratios varying in a wide range from 0.6 to 18.1%. Synthesis experiments have shown that the extent of Fe substitution in rutile varies as a function of temperature. Wittke (1967) observed the degree of Fe-for-Ti substitution in rutile to decrease from 3% for samples synthesized at 1350°C to an apparently limiting substitution of about 1% for those formed below 1000°C. In this paper it was, however, noted that the actual maximum substitution on an atomic scale could be even lower than 1%, because possibly coexisting pseudobrookite (Fe_2TiO_5) would escape detection at low concentrations. Similarly at least some of the higher substitutions reported in the literature may not be due to Fe substituting on an atomic scale, but rather, due to associated Fe-rich phases formed as a result of partial exsolution of the Fe content of more highly substituted rutiles formed at high temperatures upon cooling. Such exsolutions, leading to intergrowths of rutiles with very fine grained, Fe-rich minerals such as hematite or ilmenite have been observed in both synthetic (Yarmarkin *et al.*, 1978) and natural rutiles (Putnis and Wilson, 1978; Banfield and Veblen, 1991). Wet chemical analysis would not readily distinguish Fe contained in such microcrystalline minerals from Fe substituting in rutile on an atomic scale, so that contributions from these and similar ancillary minerals may have been attributed to rutile in the past. Electron microprobe analyses — which are much less prone to interference by such intergrowths than wet chemical analyses — of rutiles from a variety of different geological environments listed by

Rumble (1976) and Vlassopoulos *et al.* (1993) showed Fe-for-Ti substitutions averaging about 1 mole %. This value is in good agreement with the limit of substitution observed by Wittke (1967).

Because of the paucity of data on Fe in natural rutiles, only sparse information on the oxidation state of Fe in rutile exists to date. To the authors' knowledge, no Mössbauer data on natural rutiles have thus far been published, Mössbauer spectroscopic data on Fe substituting for Ti in rutile having been limited to work on synthetic samples (cf. Stampfl *et al.*, 1973; Sandin *et al.*, 1976, and references therein). The former authors showed that Fe introduced into a synthetic rutile in the trivalent state can be both readily reduced and reoxidized.

The sample studied here was collected from an abandoned rutile mine near Kragerø in southern Norway. Tröger (1935) gave the modal composition of the bulk rock, an aplitic rutile albitite locally called 'kragerøite', as 57% plagioclase ($\text{Ab}_{88}\text{An}_{12}$), 23% rutile, and < 10% each of quartz, K feldspar and ilmenite. This rock contains massive dark streaks of rutile several centimetres in size, which were mined sporadically since 1901 (Green, 1956). Material from such a streak, which X-ray diffraction showed to consist of rutile with a very minor admixture of feldspar, was ground in an agate mortar and used for study by Mössbauer spectroscopy.

Partial chemical analysis was carried out by neutron activation (NAA), and ^{57}Fe Mössbauer spectra were taken at room temperature and with the absorber cooled to 4.2 K. Isomer shifts were calculated relative to metallic Fe at room temperature, which also served for velocity calibration. The EPR measurements using a Bruker ESP380 X-band spectrometer were carried out on the original rutile at

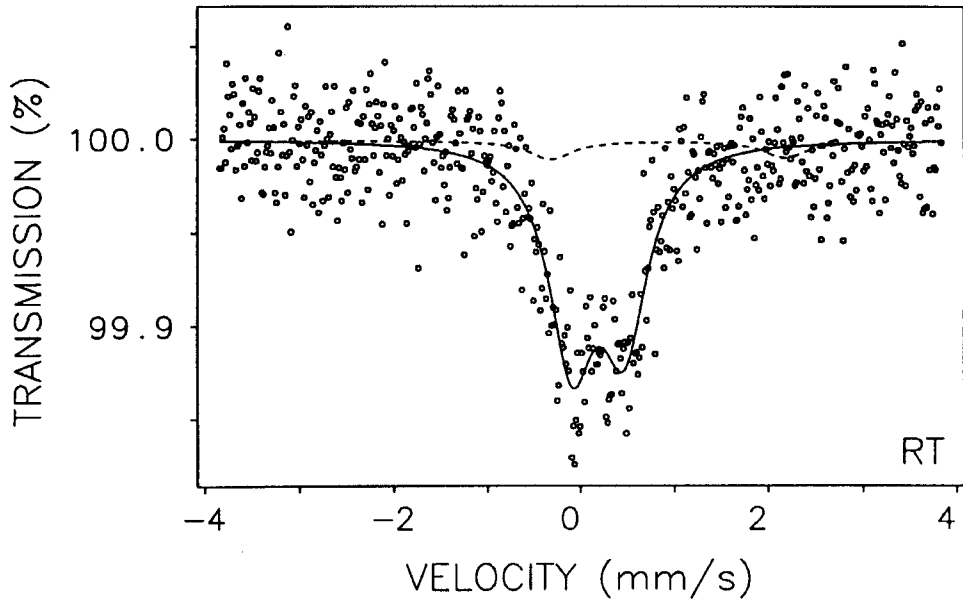


FIG. 1. Room-temperature Mössbauer spectrum of natural rutile from Kragerø fitted with one Lorentzian doublet. The broken line depicts a simulated Fe²⁺ constituent with an area amounting to 10% of that of the Fe³⁺ doublet.

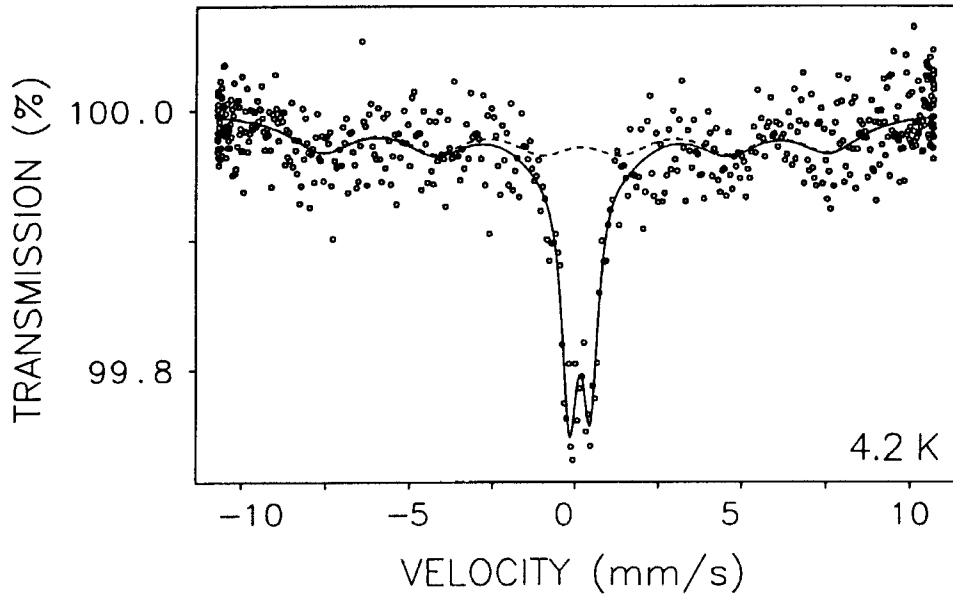


FIG. 2. Mössbauer spectrum of natural rutile from Kragerø taken at 4.2 K. The spectrum has been fitted with one sextet ensuing from slow paramagnetic relaxation (broken line) and one Fe³⁺ doublet.

TABLE 1. Room-temperature Mössbauer parameters of natural rutile from Kragerø and published values on synthetic $^{57}\text{Fe}^{3+}$ -doped rutiles

Sample	Isomer shift/Fe	Quadrupole splitting	Line width
This study (natural sample)	0.32(2)	0.56(2)	0.59(4)
Stampfl <i>et al.</i> (1973)	0.39(2)	0.69(2)	
Stampfl <i>et al.</i> (1973)*	0.44	0.30	
Sandin <i>et al.</i> (1976)	0.37(2)	0.70(3)	0.67(4)
Yarmarkin <i>et al.</i> (1978)	0.36(1)	0.54(1)	0.38(1)

All values in mm/s. Errors given in parentheses.

* single-crystal data.

room temperature and 6 K and at room temperature on a sample fired at 1000°C for three hours in air.

Results and discussion

NAA showed the studied rutile to have an Fe content of 0.24%. This corresponds to a molar Fe/(Ti + Fe) ratio of 0.41% and places the Fe content of the rutile in the lower region of the typical substitutional range outlined above. Other elements determined by NAA include 250 ppm K and 170 ppm Na, which can be attributed to the mentioned feldspar admixture, and 60 ppm Mn.

The EPR spectra showed a number of peaks that can be unequivocally attributed to substitutional Fe^{3+} and Cr^{3+} in the rutile (Eggleston *et al.*, 1981; de Biasi *et al.*, 1993). A sextet at approximately 3500 G can be attributed to Mn, but the present results do not allow a ready determination of the form of this element. To determine this and the identity of two broad features at approximately 500 and 1400 G that disappeared after firing would require further experiments with (currently not available) single crystals.

The relatively low Fe content of the rutile and the strong absorption by this mineral of the 14.4 γ ray used for ^{57}Fe Mössbauer spectroscopy precluded the registration of spectra of better quality than those shown in Figs. 1 and 2. The room-temperature Mössbauer spectrum of the rutile (Fig. 1) consisted of a doublet with parameters typical for Fe^{3+} in moderately distorted octahedral coordination (Table 1). Spectral simulation showed that the proportion of Fe^{2+} (broken line in Fig. 1) could not amount to more than 10% of the total Fe content. Published X-ray and neutron diffraction work have shown that Ti occupies a distorted, octahedrally-coordinated position in rutile (Abrahams and Bernstein, 1971; Howard *et al.*, 1991).

The liquid-helium Mössbauer spectrum was taken mainly to check for the possible presence of minor amounts of Fe-rich constituents that would escape

detection by X-ray diffraction, e.g. (superparamagnetic) hematite or (paramagnetic) ilmenite, but would give room-temperature Mössbauer spectra with lines that could be partly to extensively superimposed upon those of rutile. The spectrum taken at 4.2 K (Fig. 2) consisted of an asymmetric split spectral component with very broad lines (FWHM 2.3 mm/s) and a Lorentzian-averaged magnetic field of about 47 T. The parameters of the latter component do not correlate with any Fe-rich constituent (Fe oxide, oxyhydroxide or ilmenite) that could falsify the rutile resonance. The high line widths point to a distribution of magnetic fields rather than a discrete field, and the limiting field may well be noticeably higher than the average field of 47 T (addition of a magnetic field corresponding to the FWHM, for example, will increase the magnetic field to 54 T). Thus, although the average magnetic field is somewhat lower than that of a similar component observed by Birchall and Reid (1973) for ^{57}Fe -doped synthetic rutiles at 80 K, this component probably results, nevertheless, from slow paramagnetic relaxation due to the low structural Fe content of the rutile. This conclusion is supported by the observation that the parameters of the non-relaxing paramagnetic component at 4.2 K (Table 2) match those observed at room temperature within experimental error. The parameters of both the room-temperature Mössbauer and liquid-helium Mössbauer spectra thus are in line with the substitution of Fe^{3+} for Ti^{4+} in the rutile structure rather than forming a separate Fe phase.

Published Mössbauer data on ^{57}Fe -doped synthetic rutiles show a relatively large scatter (Table 1), with a particularly prominent discrepancy between data for powders and single crystals. These variations have been attributed to diffusion-related phenomena such as differences in stoichiometry and charge compensation mechanisms (Stampfl *et al.*, 1973). The sample from Kragerø lies within the range of variation outlined by these previous investigations. In accord with the study of Sandin *et al.* (1976) on a

TABLE 2. Mössbauer parameters of natural rutile from Kragerø at 4.2 K

Isomer shift/Fe*	Quadrupole splitting	Line width
0.26(2)	0.62(2)	0.60(6)

All values in mm/s.

* Both source and absorber cooled to 4.2 K

synthetic ^{57}Fe -doped rutile, the large line widths would indicate the existence of diverse defects that compensate for the charge imbalance ensuing from the replacement of part of the Ti^{4+} by Fe^{3+} and Cr^{3+} . This replacement may give rise to the formation of complex centres with Ti^{3+} , Fe^{4+} and Cr^{4+} , a variety of different point defects, and charge transfer phenomena (Marfunin, 1979; Kröger, 1985). Such defects are probably also responsible for the asymmetry observed by Sandin *et al.* (1976) in their Mössbauer spectrum of a synthetic ^{57}Fe -doped rutile and in the spectra described in the present paper.

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