Tungsten- and antimony-substituted rutile

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SUMMARY. Two occurrences of rutile are reported from Big Bell in Western Australia containing up to 5·8 wt % WO_3, 1·7 wt % Sb_2O_5, and 1·7 wt % FeO. One occurs in a mica schist, and the other in a pegmatite, and both contain a fine intergrowth of ilmenite lamellae. Small grains of gudmundite are associated with the rutile in the pegmatite. Microprobe analyses do not conclusively establish the mechanism of isomorphous substitution.

IT is well known that pentavalent Nb and Ta may substitute for Ti^{4+} in rutile, the excess charge being compensated by metal vacancies or a complementary amount of Fe^{2+} (Deer, Howie, and Zussman, 1962). All these ions have closely similar octahedral radii (Shannon and Prewitt, 1969). Small amounts of other ions such as Mn^{2+}, Sn^{4+}, and Pb^{2+} may also be included in the related tapiolite–mossite series. These ions are somewhat larger in radius.

This note is to report on two associated occurrences of a virtually opaque rutile phase, one from a weathered muscovite–quartz schist and one from a nearby pegmatite. Both showed appreciable substitutions of tungsten, antimony, and iron, a combination not previously observed. The former specimen was reported to have come from the spoil dump of the Big Bell Gold Mine, Coodardy, Murchison Gold Fields, Western Australia. The latter specimen from the Government Chemical Laboratories Simpson Collection, is labelled 'Rutile, Pegmatite Dyke, 400 ft level, Big Bell Gold Mine' (S4005).

Rutile from schist. The muscovite–quartz schist carries accessory andalusite and pyrite, with jarosite. The rutile occurs as small scattered grains, generally anhedral, but in grain concentrates occasional crystal faces can be seen. Grain size varies within the limits 0·02 and 0·1 mm, with most around 0·05 mm. In thin section (30 μm) the mineral is completely opaque, but in crushed grain mounts a deep violet tinge can be seen at the edges of fine splinters, and a faint pleochroism in violet tones can be detected. Optically, the mineral appears homogeneous and no difference in colour was detected between centres and edges in polished sections. Its X-ray pattern, obtained with a Guinier focusing camera, using pure thoria as an internal standard, was that of rutile with a 4·599±0·001 and c 2·9640±0·0002 Å. This represents an increase in cell volume of only 0·1 % over that of pure rutile (XRPDF, No. 21—1276). No superlattice reflections could be seen. Chemical analysis (Table I) showed the presence of appreciable amounts of tungsten, antimony, and iron (up to 8·5 % total impurity as

oxides). Electron microprobe analysis showed that the heavy metals were indeed in solution in rutile. There was often marked zoning within a grain, and Table I includes probe analyses from the edge and centre of one grain, corrected for absorption, etc., with the program MAGIC (Colby, 1968). This is an extreme example of the zoning observed, and the impurity content of the edge may be high or low. Occasional ilmenite lamellae are present within the rutile.

TABLE I. *Analyses of rutile*

	Schist			Pegmatite (S4005)	
	1	2	3	4	5
TiO_2	94·0	92·2	96·1	93·1	96·8
WO_3	2·51	5·8	1·9	4·4	1·9
Sb_2O_5	2·25	1·6	1·7	0·8	0·8
FeO	1·33	1·3	0·9	1·7	0·5
Total	100·36*	100·9	100·6	[100]	[100]
V_1	—	+4·4	+4·1	+4·6	+4·1
V_2	—	+4·1	+3·4	+3·9	+3·7

1. Bulk sample. Analyst R. Pepper. *Includes Ta_2O_5 0·17, Nb_2O_5 0·08, Cr_2O_3 0·02, and MnO, SnO < 0·01.

2 and 3. Edge and centre of grain, microprobe analysis.

4 and 5. Light and dark areas of fig. 2, microprobe analysis, normalized from multiple readings.

V_1 and V_2 are average oxidation states for (Fe, Sb, W) assuming Sb has valence of +5 and +3 respectively. For discussion, see text.

*Rutile from pegmatite.* Simpson (1952) reports that

mica schist . . . exposed in the open-cut at the Big Bell Gold Mine is traversed with innumerable minute quartz veins, and a few small veins of pegmatite. Associated with the latter the Author [Simpson] found a black well-crystallized mineral, which proved to be nigrine, and which contained about 97 % TiO_2. Masses ranging from 1 oz–1 lb in weight were collected. Some of the large crystals were twinned on (101) and were striated parallel to a and m. Faces developed were a, m, e, s, the cleavages were m and a, and specific gravity 4·29.

The specimen we have examined (S4005) is part of a crystal originally over an inch across, with well developed pyramidal and prism faces. The mineral is more transparent than that in the schist, with a similar pleochroism, but both features can only be detected in finely crushed material. Ilmenite lamellae a few μm thick can be observed in two orientations in most areas of the polished section (fig. 1) and one small region exhibits twinning on two planes.

The accessory minerals are of great interest since they include the rare iron–antimony sulphide, gudmundite. This is the analogue of arsenopyrite, which also occurs in the specimen. One large grain of the latter, in contact with the gudmundite, has inclusions of sphalerite. This assemblage is consistent with the stability conditions for gudmundite described by Barton (1971). A number of small grains of scheelite were recognized in gangue areas within the rutile, and it is an interesting coincidence that this new occurrence of gudmundite, like that at Beira Baixa (Clark, 1966) should be associated with

high tungsten values. Gudmundite has not been successfully synthesized, and it seems possible that the presence of tungsten stabilizes its structure; the gudmundite in our sample contained perhaps 0·2 % W. Cracks in the rutile were largely filled with calcite and poorly crystallized sphene.

Microprobe examination showed that the pegmatite rutile contained the same substitutions as the rutile from the schist. The composition was much more uniform for the former, although some tungsten-rich areas could be observed using the scanning mode of the electron microprobe (fig. 2). Table I gives average compositions of the light and
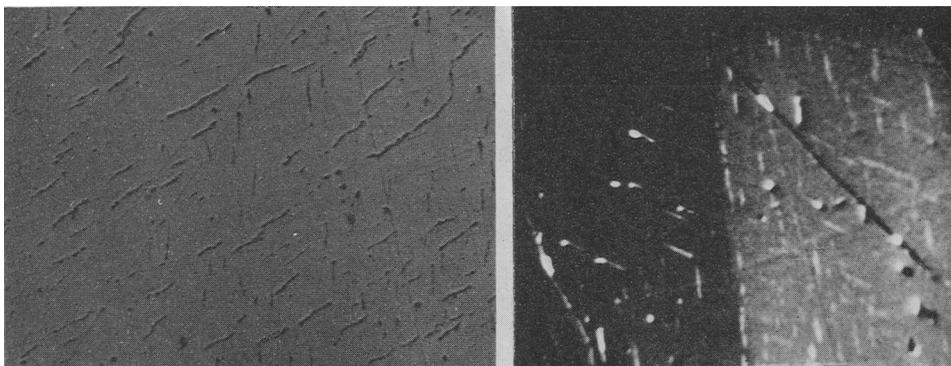
FIGS. 1 and 2: FIG. 1 (left). Polished section (approx. (311)) of rutile from pegmatite, showing ilmenite lamellae. Width of field c. 560 μ. FIG. 2 (right). Backscattered electron image of rutile from pegmatite. The light areas contain approximately 4·4 % WO_3, and the darker areas approx. 1·9 % WO_3. Width of field c. 900 μ.

dark regions of the figure, which are respectively high and low in tungsten. A large number of partial analyses showed that the tungsten content varied from 1·5 % to 7·3 % WO_3, and antimony from 0·7 % to 1·2 % Sb_2O_5. The minimum value for FeO was 0·3 %, but a maximum cannot be obtained owing to interference from ilmenite lamellae. The values in Table I are representative of the two compositions that seem to be preferred. The ilmenite lamellae contain little or no tungsten and no antimony.

Discussion. The question of stoichiometry and the valence states of the various ions is interesting and important. It is known that $FeSbO_4$ has the rutile structure, and this would require Fe^{3+} and Sb^{5+}. The octahedral radii are most similar for Ti^{4+} (0·605 Å), W^{6+} (0·60 Å), Sb^{5+} (0·61 Å), and Fe^{2+} (0·61 Å) (Shannon and Prewitt, 1969), and this assignment would explain the close similarity of the lattice spacings to those of rutile. Because of the difficulty of dissolving the rutile without oxidation of the iron, and the variable valence of the other metal ions, it is not easy to confirm the presence of Fe^{2+}. The presence of ilmenite lamellae means that some Fe^{2+} has existed in the rutile at some stage, but the Mössbauer spectrum[1] of a purified powder sample is inconclusive. As it happens, the average valence of the dissolved ions is in most cases too high, even assuming Fe^{2+}, so this is the most probable state of the iron.

[1] By courtesy of Dr. J. Ward, CSIRO, Division of Mineral Chemistry.

The evidence for Sb^{5+} rests almost entirely on the size of the ion. Sb^{3+} is approximately 30 % larger, and would have difficulty entering the lattice. If it did enter into solid solution it would produce an appreciable dilation. In Table I average oxidation states for the impurity ions are given on the assumptions that Sb is 3-valent (V_2) and 5-valent (V_1) respectively. It will be noted that V_1 corresponds to a metal-deficient rutile phase and in most instances, V_2 indicates metal excess. V_1 is reasonably close to MO_2 stoichiometry for the low-tungsten areas and V_2 for the high-tungsten areas.

If Sb^{5+} and Fe^{2+} coexist in the structure, some form of environmental stabilization of these valence states must operate (Nyholm and Tobe, 1963). In a similar way, Tb^{4+} and Tu^{2+} are thought from spectroscopic evidence to coexist in solid solution in zircon (Bershov, 1971). Other unusual ionic pairs have been observed, such as Cu^+ and Fe^{3+} in delafossite (Widersich *et al.*, 1968), and Fe^{3+} and Ti^{3+} (Strens, 1967).

Interestingly enough, similar problems arise in the ilmenorutiles, which also in many cases show the reticulate intergrowth structure of ilmenite within the rutile matrix (Vlasov, 1964), and where sphene may also occur in the margins. Vlasov states that 'no definite stoichiometric relationships are noted between the components Ti, Nb, Ta, and Fe'. As in the present system, a greater substitution of higher-valent ions seems to be associated with a higher concentration of ilmenite lamellae. Perhaps in each case, the concentration of iron into the ilmenite lamellae has resulted in the metal-deficient rutile phase.

The chemical similarity of the two forms of rutile at Big Bell suggests a common origin, though the actual formation was probably different. The 'pegmatite' seems the logical source for the antimony and tungsten and possibly the titanium. However, the limited data indicate that the rutile of the metasediment has a higher heavy metal content than the pegmatitic phase. Sulphurization of ilmenite commonly results in rutile formation (Ramdohr, 1969), and if sulphur was accompanied by tungsten and antimony, this might offer an alternative mechanism to direct introduction as a pegmatitic phase, although the ilmenite lamellae appear to be a precipitation phenomenon rather than a residual feature.

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