

matters arising

Green rust: a pyroaurite type structure

MCGILL, MCENANEY AND SMITH¹ have described a green corrosion product of iron developed in water containing NaCl, K₂SO₄, NaCO₃, mixtures of these salts, and NaOH under various degrees of aeration. The X-ray data they reported indicate that the product is a member of the pyroaurite group²⁻⁴. In fact, Stampfl⁵ and Taylor⁶ have also concluded that a ferrous-ferric green rust material belongs to the group of pyroaurite structures.

We have been concerned⁷ with the synthesis of products similar to the mineral takovite which has a formula of the pyroaurite type near to (Ni,Mg)₆(Al,Fe³⁺)₂(OH)₁₆CO₃·4H₂O. We find that such products are formed readily in solutions containing Cl⁻, NO₃⁻ and SO₄²⁻ ions, provided that CO₂ is not rigorously excluded. When water in its normal state or saturated with CO₂ is used, the same or similar final product is obtained. The presence of the anion CO₃²⁻ is shown unambiguously by infrared spectroscopic data. We suspect that other anions play only a small role in the formation of the product when CO₃²⁻ ions are present. For reasons which are not entirely clear, the pyroaurite structure type seems to form very readily when CO₃²⁻ ions are available. Possibly the planar nature of the CO₃²⁻ ion and the total number required are favourable factors; NO₃⁻ ions, although planar, must be twice as numerous for electrical neutrality.

Using the X-ray data reported by McGill, *et al.*¹, we have recalculated the unit cell parameters using the refinement program of Evans *et al.*⁷; the results are: $a = 3.166 \pm 0.001$, and $c = 22.52 \pm 0.01$ Å—values which are close to those given by McGill *et al.* and also by Stampfl⁵: $a = 3.17$; $c = 22.8$ Å.

It is of interest to consider a possible relationship between cation composition (as indicated by the weighted mean cation radius, \bar{r}), and the hexagonal a parameter. Figure 1 shows such a plot with data taken from the literature, including two unpublished points (G.W.B. and D.L.B.), dealing with takovite. The \bar{r} values are calculated using the crystal radii of Shannon and Prewitt⁸. The smallest value of \bar{r} is for takovite (G.W.B. and D.L.B., unpublished) and the largest for the green rust studied by Butler and Benyon⁹ on the assumption of a 3 : 1 ferrous-ferric ratio. The available data cluster near to a

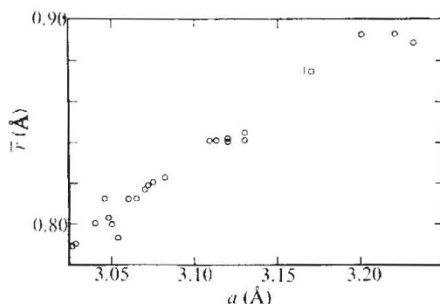


Fig. 1 Plot of \bar{r} (mean cation radius), against unit cell parameter a for pyroaurite-type structures. Vertical line indicates the a parameter of the green rust of McGill *et al.*¹.

straight line and indicate for the green rust of McGill *et al.* a ferrous-ferric ratio of about 2:1; the precise result depends on how the line is drawn. In future studies of pyroaurite group materials, it will be useful to have chemically analysed materials and accurate cell parameters so that a composition-cell parameter graph can be drawn with greater accuracy than is now possible.

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AN extraordinary orientational relationship between the rhombohedral green rust (with hexagonal unit cell dimensions $a = 3.181$ Å and $c = 21.82$ Å) and magnetite (cubic with $a = 8.434$ Å)—namely, $[1\bar{1}\bar{1}]_{rh}$ or $[42\bar{1}]_{hex} // [1\bar{1}\bar{1}]_{cub}$; and $(566)_{rh}$ or $(1\ 0\ \bar{1}\ 17)_{hex} // (1\bar{1}\bar{1})_{cub}$ —has been reported by McGill, McEnaney and Smith¹. I should like to query this result, and to suggest that there is really no evidence that the relationship is other than $[00.1]_{hex}$ or $[111]_{rh} // 111_{cub}$, and $(3030)_{hex}$

or $(2\bar{1}\bar{1})_{rh} // (112)_{cub}$, as would be expected from a comparison of the oxygen packings of the two structures.

If the material is not well crystallised, or the platelet is very thin, the reciprocal lattice points will be extended parallel to $[00.1]_{hex}$ and it will not then be necessary to postulate that the diffraction spots, visible in their Fig. 1 and obtained when the beam is perpendicular to the crystal flake, have indices which strictly obey the requirement $-h+k+l = 3n$. The photographs reproduced in ref. 1 do not seem to show departures from hexagonal symmetry. Moreover, the hexagonal and rhombohedral cell dimensions are not entirely consistent with each other and the sets of planes considered to be equivalent do not really have similar d -spacings.

The simpler topotactic relationship had been reported earlier^{2,3} but, together with work on the structure of the green rust materials⁴, had gained inadequate publicity.

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MCGILL ET AL. REPLY—Mackay's argument¹ presumes that there is close matching of oxygen ions in the green rust and magnetite structures resulting from a topotactic transformation, that is, internal atomic displacements resulting in accord in three dimensions between initial and final lattices². There is no conclusive evidence for this type of transformation from our experiments on the corrosion of cast iron. It has been found that magnetite and green rust usually precipitate from solution independently of each other, although there are isolated examples of the epitaxial growth of magnetite on green rust from solution. Figure 3 of our original contribution³ illustrates this, and shows magnetite as three-dimensional, 'island' outgrowths from the surface of green rust crystals, a morphology commonly observed in epitaxy. Close matching of oxygen ions between green rust and magnetite is not, therefore, a necessary condition, since epitaxy can occur with large degrees of atomic