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# THE GREEN COLOR OF CERTAIN FERROUS MINERALS

GERALD R. MACCARTHY, *University of North Carolina*

In two earlier papers[1] the writer has attempted to show that iron silicates exist in four important color modifications; i.e., colorless ferrous compounds, blue hydrous ferro-ferric compounds, gray or black anhydrous ferro-ferric compounds, and red and yellow ferric compounds. Both in the case of natural minerals and of artificial compounds it was shown that blues are apparently in all cases due to the presence of a hydrous double salt, both ferrous and ferric iron being present. Also evidence that iron greens are in reality mixtures of iron blues and iron yellows was presented. These different types of iron compounds are well represented in the mineral world and almost all minerals colored by iron may be fitted into one or another of the above groups.

The relative "ferrousness" of an iron-bearing substance may be expressed by means of its "ferro-ferric ratio," a numerical expression obtained by dividing the percentage content of ferrous oxide by the percentage content of ferric oxide. Materials high in "ic" iron therefore have a low ferro-ferric ratio, while for materials rich in "ous" iron this ratio is high. When the word "ratio" is used in the following discussion "ferro-ferric ratio" is to be understood.

During the course of the experimental work described in the earlier papers it was found that decided iron greens were developed only in such artificial compounds and mixtures as possessed comparatively low ratios. In other words, this color was found only in substances which were essentially ferric but which at the same time contained some ferrous iron. Thus greens developed in silicate mixtures only between ratios 0.60 and 0.70.

When these artificial compounds were compared with a series of green rocks and minerals some rather striking differences were

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[1] *J. Elisha Mitchell Sci. Soc.*, **41**, 135 (1925), and *Am. J. Sc.*, **12**, 17 (1926).

found. In the natural minerals the average ratio was much greater than unity, in the artificial compounds much less than unity. The former are then chiefly ferrous, while the latter are predominately ferric. Although it appears that the majority of green rocks and minerals are distinctly ferrous, yet this is by no means always true, a fair number of ferric ones being evident.

In the ferric group we find such minerals as glauconite,[2] with a ratio of 0.082 (average of 6 analyses), serpentine[3] with a ratio of 0.759 (average of 5 analyses), dufrenite with a ratio of 0.076 (average of 3 analyses) two augites with an average ratio of 0.900 etc.

In the ferrous group we find such minerals as diopside with a ratio of 7.43 (average of 4 analyses), amphibole with a ratio of 4.21 (average of 5 analyses), two green biotites with an average ratio of 2.71, etc. The chlorites are almost entirely ferrous, having in very few cases ratios less than unity. Clinochlore[3] has a ratio of 2.57 (average of 7 analyses), prochlorite a ratio of 17.82 (average of 5 analyses), thuringite a ratio of 2.77 (average of 4 analyses), etc. Olivine is decidedly ferrous in character but enough nickel to affect its color is so often present that it seems best to omit this mineral from the discussion.

Among the non-igneous rocks are found one green sandstone with a ratio of 3.39, and thirteen green slates with an average ratio of 3.75. The green color of most, if not all, green slates seems to be due to chlorite,[4] the ratio being perhaps somewhat affected by other iron bearing minerals (such as hematite) also common in such rocks.

In making the artificial green compounds which were studied three different methods of procedure were employed; partial reduction of a ferric salt, partial oxidation of a ferrous salt, and direct precipitation from solutions containing ferric and ferrous salts which were not mutually reactive, but which would react with the precipitant to form a ferro-ferric salt. Under the con-

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[2] The analyses from which the following ratios were computed are taken chiefly from Dana's SYSTEM OF MINERALOGY, 6TH ED., and from *Bull.* **591,** *U.S.G.S.* The glauconite analyses are from Collet's LES DÉPÔTS MARINS, p. 165.

[3] One a typical analysis was omitted in computing the average.

[4] Renard, quoted by Dale in *Bull.* **275,** *U.S.G.S.*, p. 12, lists the minerals found in green slates in the following order: quartz, muscovite, chlorite, hematite, and rutile. Since chlorite is the only green mineral reported it is apparently responsible for the green hue of the rock.

ditions of the experiments the various compounds produced were either in solution or else were in the form of moisture laden colloidal or near colloidal precipitates, and under these conditions the production of mixtures containing ferric, ferrous, and ferro-ferric compounds proved impossible. However, mixtures of ferric and ferro-ferric and of ferrous and ferro-ferric compounds were obtained freely.

The solutions and colloidal precipitates could readily recombine to form new compounds so that should any ferric iron be present it would immediately unite with any ferrous iron also present to form a compound of the ferro-ferric type. If ferrous iron were in excess the final mixture would be composed of ferrous and ferro-ferric salts; if ferric iron were in excess a mixture of ferric and ferro-ferric salts would result, no mixture composed of more than two different types of compounds being obtained. Mixtures of a yellow ferric and a blue (hydrous) ferro-ferric compound of necessity would appear green and since in such mixtures ferric iron exceeds the ferrous iron the ratio is always low. The other type of mixture obtained—ferrous and ferro-ferric—consisted of a colorless ferrous and a blue (again hydrous) ferro-ferric salt and hence was always some shade of blue. Since ferrous iron predominates in such mixtures the ratio is always greater than unity.

If, during the growth of a mineral whether from a magma or from solution, both ferric and ferrous iron were present any iron silicate which might form would, just as in the case of the artificial compounds, consist either of a mixture of a ferro-ferric and a ferric or of a ferro-ferric and a ferrous salt, the type of mixture being dependent upon which type of iron was present in the greater amount. And as in the case of the artificial compounds, no green mineral with high ratio could form. Blue ferrous minerals might however be expected, and are in fact not at all rare. Among such minerals are vivianite, blue vesuvianite, iolite, crocidolite, glaucophane, blue calcite, and the like.[5] Green minerals of low ratio (rich in ferric iron) might likewise be expected under these conditions. Nevertheless many distinctly ferrous minerals are green in color, and it is the purpose of this paper to point out a possible origin of this phenomenon.

As is noted above, artificial green compounds were produced by a partial reduction of ferric salts and by a partial oxidation of

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[5] *Am. J. Sci.*, **12,** 19–20 (1926).

ferrous salts as well as by direct precipitation. For example, partial oxidation of a blue ferro-ferric silicate causes the formation of a yellow ferric silicate and the mixture of the two, by the law of color mixture, gives a green hue to the substance. Partial oxidation of a colorless ferrous silicate first produces a blue ferro-ferric silicate and after further oxidation a yellow ferric silicate is also obtained. The mixture thus obtained contains blue ferro-ferric and yellow ferric silicates, and again appears green. In the same way the partial oxidation of a ferrous silicate mineral would produce blue and green colorations. But one difference between the behavior of the artificial compounds and of well crystallized minerals immediately appears. In the former, as has been pointed out, recombination easily takes place, so that ferric and ferrous compounds would not be stable in the presence of each other, and no green color could develop until almost, if not all, of the ferrous iron had entered into ferro-ferric compounds. In a solid crystal we find a different state of affairs. Here the constituent particles are held so firmly by the restrictions of the space lattice that much recombination without a simultaneous reorganization of the space lattice and consequent destruction of the original crystal could not take place. Although partial oxidation of a ferrous crystal could well transform certain of the iron atoms into the ferric state such ferric atoms could not change their positions as long as the original space lattice remained intact, and would not join their ferrous neighbors to form a ferro-ferric molecule. In this case all three types of iron compounds might exist side by side,—first, remnants of the original ferrous material, colorless and hence of no effect on the general color of the crystal;[6] second, blue ferro-ferric molecules; and third, yellow ferric molecules. Such a mixture would have a high ratio because of the ferrous iron it contained and at the same time would possess a decided green color due to the blue and yellow of the ferro-ferric and ferric molecules also present.

Since the color of iron compounds is very intense only an extremely small proportion of the iron need be in other than a ferrous condition for a noticeable color to develop. Hence only a slight degree of oxidation is called for. In a like manner a slight reduction of an originally ferric silicate might cause a green color to develop

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[6] Colorless ferrous minerals are represented by some non-ferric vivianites and siderites. See Dana, 6th ed., pp. 277 and 815.

but, since dominantly ferric minerals can possess a green color even when directly precipitated from solution there is no point in following this particular phase of the problem further.

It is ordinarily considered that even such a mild oxidation or reduction as is here called for would cause a breaking down of the structure of the original crystal with a parallel development of "alteration products" and such is doubtless often the case. However, Winchell[7] has suggested on other grounds that such changes in the state of oxidation of the iron may sometimes take place without destruction of the crystal structure, his remarks applying specifically to chlorite. The experiments of Watson on partial oxidation of vivianite[8] also indicate such a possibility.

It is rather suggestive to note that the majority of green iron bearing minerals of high ratio are not those most common at great depths but rather those common at depths within the reach of atmospheric oxygen. Examples of such minerals are the chlorites, green vivianite, uralite and the like. Most of these minerals are in themselves "alteration products" and hence have passed through changes which might well include some slight degree of oxidation. On the contrary, the green iron-bearing minerals of low ratio are usually those which are formed in the greater depths or in other situations such that an increase in oxidizing conditions is not likely to occur after formation of the mineral. Among such deep-seated minerals are the green garnets, certain augites, etc. Glauconite appears to have formed directly from mixed solutions containing both ferrous and ferric iron with the latter present in greater amount, and hence resembles the artificial compounds in mode of origin. Dufrenite, often associated with glauconite, may well be of similar origin.

SUMMARY. It appears very probable that most green *ferric* minerals originated as such, although some may have suffered subsequent partial reduction, but that the green color possessed by certain *ferrous* minerals is a secondary development and is always caused by a partial oxidation of already crystallized material.

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[7] *Am. J. Sci.*, **11,** 283 (1926).

[8] *Am. Mineralogist,* **3,** 159 (1918).