TECHNICAL PAPERS

The Nature of the Iron Compounds in Red and Yellow Sandstone[1]

L. J. E. HOFER and SOL WELLER

Central Experiment Station,
Bureau of Mines, Pittsburgh, Pennsylvania

The color of sandstone usually is due to some form of iron which was probably deposited in the sandbeds from chalybeate water—for example, an aqueous solution of ferrous bicarbonate. Rayleigh (3) has demonstrated geologically probable conditions by which both red and yellow pigments can be formed from chalybeate water. Using these conditions, he has prepared both synthetic red and synthetic yellow sandstones. Both the red and the yellow pigments were demonstrated to be iron oxides or oxide hydrates with variable amounts of water. Rayleigh did not consider the difference in water content between the red and the yellow to be significant so far as color is concerned. The present paper deals with the identity of these pigments.

Rayleigh observed that chalybeate water standing undisturbed, exposed to the air, will simultaneously form both the red and the yellow oxide; the former develops as a skin upon the surface, whereas the latter forms a precipitate in the body of the solution. Formation of the red oxide is favored by increasing the area of air-solution interface; formation of the yellow oxide, by bringing more air into solution in the chalybeate water. By exposing sand moistened with chalybeate to air at 50°C., a red synthetic sandstone was obtained; but by exposing sand submerged in chalybeate water to air at the same temperature, a yellow synthetic sandstone was formed.

The oxidation of ferrous bicarbonate solutions has been studied previously by Albrecht (1), Schikorr (4), and Baudisch and Albrecht (2), all of whom agree that when undisturbed ferrous bicarbonate solutions oxidize, a crust of brown material forms on the surface while a yellow precipitate deposits in the bulk of the solution. The similarity in the manner of formation indicates beyond doubt that the brown and yellow oxides of these authors are identical or closely related to the red and yellow oxides of Rayleigh. X-ray diffraction patterns showed the brown oxide to be $\gamma Fe_2O_3 \cdot H_2O$ (lepidocrocite) and the yellow oxide to be $\alpha Fe_2O_3 \cdot H_2O$ (goethite). Normally both $\gamma Fe_2O_3 \cdot H_2O$ and $\alpha Fe_2O_3 \cdot H_2O$ are yellow (5); but $\gamma Fe_2O_3 \cdot H_2O$ is quite unstable, decomposing to γFe_2O_3 (maghemite-red) even at 100°C. The γFe_2O_3 so formed is itself metastable and can decompose to αFe_2O_3 (hematite-red). The color of the brown or red oxide observed by these authors is thus probably due to partial decomposition of $\gamma Fe_2O_3 \cdot H_2O$. The oxidation of ferrous bicarbonate solutions containing low concentrations of CO_2 favors the formation of $\gamma Fe_2O_3 \cdot H_2O$ in bulk rather than $\alpha Fe_2O_3 \cdot H_2O$ (3). This may explain why γ- rather than $\alpha Fe_2O_3 \cdot H_2O$ forms in the surface of oxidizing chalybeate water.

To check and extend these conclusions about Rayleigh's oxides, samples of both the red and the yellow oxides were made up according to his directions and studied by X-ray diffraction and the magnetic balance. Chalybeate water was prepared by bubbling CO_2 through distilled water in contact with high-purity iron shavings. The solution as used contained 0.655 gram Fe_2O_3/l. The yellow oxide was prepared by simply bubbling air through the solution and filtering and drying the precipitate. The red oxide was made by dropping the chalybeate water on a slowly rotating glass cylinder, which was dried by a hot plate. The temperature of the cylinder was kept well below 100°C. The red deposit so formed was scraped from the cylinder and used without further treatment.

X-ray diffraction patterns of the yellow oxide proved it to be mainly $\alpha Fe_2O_3 \cdot H_2O$. The magnetic susceptibility was 83×10^{-6} c.g.s. units/gram—in fair agreement with that of $\alpha Fe_2O_3 \cdot H_2O$ and $\gamma Fe_2O_3 \cdot H_2O$, both of which have susceptibilities of 42×10^{-6}. On heating the sample to 200°C. for about two hours, the susceptibility rose to $1,200 \times 10^{-6}$, indicating the presence of some $\gamma Fe_2O_3 \cdot H_2O$, which decomposes to ferromagnetic γFe_2O_3. X-ray diffraction patterns of the red oxide showed the presence of hematite and small amounts of γFe_2O_3. The magnetic susceptibility was $2,200 \times 10^{-6}$ as compared with 22×10^{-6} for hematite. The magnetism, readily demonstrated with a small permanent magnet, is undoubtedly due to γFe_2O_3.

Through the courtesy of David M. Seaman, of the Carnegie Institute, a series of sandstones were obtained for study. A specimen of red St. Peter's sandstone from Mineral Point, Wisconsin, contained 0.32 per cent iron as Fe_2O_3 and had a gross magnetic susceptibility of about 5×10^{-6}. The sand itself is almost pure quartz, as is shown by the fact that extraction with warm 1:1 HCl leaves a white product whose diamagnetic susceptibility ($X = -0.43 \times 10^{-6}$) is nearly the same as that of pure quartz ($X = -0.49 \times 10^{-6}$). The iron oxide in the sample thus must have a susceptibility of $1,600 \times 10^{-6}$. Such a high susceptibility could have originated only with γFe_2O_3. Since γFe_2O_3 is metastable with respect to αFe_2O_3 (paramagnetic, $X = 22 \times 10^{-6}$), this high susceptibility should be lowered on heating to 500°C. This was found to be the case; the gross susceptibility for the heated sandstone was only 0.76×10^{-6}, corresponding to an oxide susceptibility of 230×10^{-6}. Of the several other sandstones examined, all had susceptibilities far greater than could be attributed to hematite, goethite, or lepidocrocite; but unfortunately, the sandstones, after acid extraction, still had appreciable paramagnetic susceptibilities, and the results could not be so clearly interpreted as in the case of St. Peter's sandstone. The susceptibilities were measured in a field strength of 2,500 gauss.

References

1. ALBRECHT, W. H. *Ber.,* 1929, 62, 1475.
2. BAUDISCH, O., and ALBRECHT, W. H. *J. Amer. chem. Soc.,* 1932, 54, 943.
3. RAYLEIGH, LORD. *Proc. roy. Soc.,* 1946, 186A, 411.
4. SCHIKORR, G. Z. *Anorg. allg. Chem.,* 1930, 191, 332.
5. WEISER, H. B. *Inorganic colloid chemistry.* Vol. II: *The hydrous oxides and hydroxides.* New York: John Wiley, 1935. Pp. 27–44.