assemblage on the adit dump is similar to that at Pen-y-bwlch shaft; it includes wulfenite and, in addition, some calcite. Pyromorphite and secondary copper minerals, but no wulfenite, were found on the dumps of Taylor's shaft itself.

The wulfenite crystals, 0·2–1 mm in size, are of three habits: very thin clear yellow rectangular plates (from dump A); groups of clear honey-brown thick bevelled plates (dump B); and orange-brown translucent elongated bipyramids with convex curved edges (dumps A, B, and C).

Secondary minerals were identified by their infra-red spectra, and the identity of the wulfenite was confirmed by an X-ray powder photograph kindly taken by Miss E. E. Fejer of the British Museum (N.H.).

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Coexistence of 'incompatible' ions and concentration processes in two mineral systems

Manganese in mineral analyses is commonly stated as MnO when FeO is present, on the grounds that the oxidation of Fe^{2+} by Mn^{3+} in solution indicates instability of this ion-pair in the solid also, and a similar assumption is usually made regarding the pair Ti^{3+}–Fe^{3+}, again on the basis of their behaviour in aqueous solution. Neither assumption rests on a sound theoretical basis, and it is not therefore surprising that exceptions to both have recently been described. Smith and Albee (1965) give analytical data for an equilibrium piemontite–garnet assemblage in which Fe^{2+}, Fe^{3+}, Mn^{2+}, and Mn^{3+} coexist (Mn^{3+} and Fe^{3+} in the piemontite, Fe^{2+}, Fe^{3+}, and Mn^{2+} in the garnet), but were unable to account for the observation, and Chesnokov's (1959) work on the absorption spectra of titanaugites, confirmed and extended by Burns (unpub.), has shown that Fe^{3+} and Ti^{3+} coexist in these minerals.

Nature of species in solution. In any solution, whether solid solution, aqueous solution or silicate melt, equilibria exist between the various oxidized and reduced species, the relative concentrations of which are given by the Boltzmann relation: $n_{\mathrm{ox}}/n_{\mathrm{red}} = \exp(-\Delta E/RT)$, where ΔE is the energy difference, taken with its proper sign, between the oxidized and reduced states. For example, conductivity measurements by Lotgering (1964) have shown that in a manganese ferrite solid solution: $\mathrm{Mn}^{2+}+\mathrm{Fe}^{3+} \rightleftharpoons \mathrm{Fe}^{2+}+\mathrm{Mn}^{3+}$; $\Delta E = (+)\,0{\cdot}30$ eV. Thus activities of Mn^{3+} and Ti^{3+} in natural solutions are finite, even in the presence of excess Fe^{2+} and Fe^{3+} respectively, and trace amounts of these 'unstable' ions will inevitably be incorporated in phases crystallizing from these solutions.

Nature of the concentration process. The availability of small amounts of Mn^{3+} and Ti^{3+} in solution does not in itself account for the crystallization of phases containing $\mathrm{Mn_2O_3}$ and $\mathrm{Ti_2O_3}$ as major components from systems containing significant Fe^{2+} and Fe^{3+} respectively. Consider the following crystallization–solution cycle applied to a phase separating from a solution containing Fe^{2+}, Fe^{3+}, Mn^{2+}, and Mn^{3+} in their equilibrium proportions:

$$\begin{tikzcd}
{[\mathrm{Mn}^{2+}, \mathrm{Fe}^{3+}]_s} \arrow[rr, "\Delta G_{12}"] & & {[\mathrm{Mn}^{3+}, \mathrm{Fe}^{2+}]_s} \arrow[dl, "\Delta G_{23}"] \\
& {[\mathrm{Mn}^{3+}]_c[\mathrm{Fe}^{2+}]_s} \arrow[ul, "\Delta G_{31}"] &
\end{tikzcd}$$

The condition for Mn^{3+} to be concentrated in the crystals is simply that ΔG_{23} be negative, but large amounts of Mn^{3+}, requiring extensive oxidation of Mn^{2+} by Fe^{3+} will enter the crystals only if ΔG_{31} is small or positive, when Mn^{3+} will enter the crystals until: $[\mathrm{Mn}^{3+}]_c/[\mathrm{Mn}^{2+}]_s = \exp(-\Delta G_{31}/RT)$.

Inspection of this cycle shows clearly that the degree to which an ion is concentrated in the crystals is dependent on both G_s and G_c terms, and that it is therefore incorrect to consider the distribution of an ion between solid and liquid phases in terms of bonding in the crystal alone —a practice still followed by many geochemists, but recently criticized by Burns and Fyfe (1966). The result is general, and can be applied to other concentration processes.

Discussion. The nature of factors influencing the sign and magnitude of ΔG_{31} may be illustrated by reference to the concentration of Mn^{3+} in piemontite and viridine, and of Ti^{3+} in titanaugite.

The concentration of Mn^{3+} in piemontite and viridine is probably linked with the pre-existing tetragonal distortion of the (AlFe) and

AlOH sites in the epidote structure (Strens, 1965, 1966; Burns and Strens, 1967), and of the Al site in viridine (Strens, unpublished). These distortions stabilize the Mn^{3+} ion by 15 to 20 Kcal/mole relative to Mn^{3+} in an undistorted octahedral site. Similar crystal-field effects may be expected in compounds of Cr^{2+} and Cu^{2+}, and to a smaller extent with other transition-metal ions.

The concentration of Ti^{3+} in titanaugite may be a more complex process. Titanaugites are commonest in high-temperature silica-deficient rocks, in which the replacement of Si by Al is greatest. Charge compensation then requires replacement of Mg by a trivalent ion, and size considerations suggest that this should be Fe^{3+} or Ti^{3+} rather than Al (compare stability of acmite, instability of jadeite at low pressures).

Oxygen partial pressure will also be critical in determining the activities of Mn^{3+} and Ti^{3+}, but it follows from the discussion above that minerals containing 'Mn_2O_3' and 'Ti_2O_3' have not necessarily crystallized within the stability fields of these oxides.

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BOOK REVIEWS

King (L. C.). *Morphology of the earth* (2nd edition). Edinburgh (Oliver & Boyd), 726 pp., 247 figs. Price: 105*s*.

Professor King's book has undergone only minimal revision in its new edition, the most important changes amounting to a few additional paragraphs in certain sections. The subject matter, layout and figures are almost identical to those of the 1962 edition, and the over-all