

# OXIDE ZONE GEOCHEMISTRY

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out on the basis of estimated free energies of formation and it is clear that here is a case where more experimental work is required. This is particularly pertinent in view of the conclusion that the mineral plumbogummite,  $PbAl_3(PO_4)_2(OH)_3 \cdot H_2O$ , may control the solubility of lead in the natural environment where phosphate and aluminium are both present, including roadside environments contaminated with lead by the burning of leaded petrols.

Another conclusion is evident from a consideration of the equilibrium constant values for (11.1) with respect to pyromorphite and mimetite. Within experimental error, the solubilities of the two minerals are the same. Thus it would be expected that the two minerals would exhibit solid solution characteristics, especially in view of the fact that the  $PO_4^{3-}$  and  $AsO_4^{3-}$  ions have the same charge, about the same size (238 and 248 pm, respectively) and virtually the same conjugate acid  $pK_a$  values. Indeed, solid solution phenomena between the two end-members have long been appreciated [1], and extend to other members of the group of minerals which have comparable stoichiometries, such as chloropyromorphite,  $Cu_3(PO_4)_2Cl$ , and vanadinite,  $Pb_3(VO_4)_2Cl$ .

In order to illustrate this phenomenon, it is necessary to restate the conditions which need to be examined. Distribution coefficients are especially important in this regard. With respect to the pyromorphite-mimetite solid solution we may write equation (11.5), derived from (11.1), where  $K'$  is  $K^{(1)}$  (11.1),  $N_i$  is the mole fraction of the component in the solid solution and  $\gamma_i$  is its activity coefficient.

$$K'(\text{pyro})/K'(\text{mim}) = \frac{[H_2PO_4^-]N_{\text{mim}}\gamma_{\text{mim}}}{[H_2AsO_4^-]N_{\text{pyro}}\gamma_{\text{pyro}}} \quad (11.5)$$

A simplification introduced here is that for any ionic strength, the activity coefficients of the  $H_2PO_4^-$  and  $H_2AsO_4^-$  ions (or any other related pairs) are equal by virtue of their chemical and physical similarities. At 25°C, the left-hand side of (11.5) is equal to 1, and so the distribution coefficient given in (11.6) is a measure of the ratio of the solid-state activity coefficients for the solid solution.

$$K^{(1)} = \frac{[H_2PO_4^-]N_{\text{mim}}}{[H_2AsO_4^-]N_{\text{pyro}}} \quad (11.6)$$

The distribution coefficients have been measured over the full range of compositions [10], and are equal to 0.99(5). This value is really equal to unity and thus it is apparent that the solid solution behaves ideally. However, two caveats need to be mentioned. First, the end-members are isostructural but not isomorphous. Pyromorphite is hexagonal, space group  $P6_3/m$ , and mimetite is monoclinic, space group  $P2_1/b$ . The structures are closely related, however, and despite this formal symmetry distinction, it is clear that the lattices of the solid solutions reflect the availability of the phosphate and arsenate ion in solutions from which the solid phases crystallize. This is also true at higher pH [10] when the  $HXO_4^{2-}$  ions are considered; the appropriate distribution coefficient is equal to 0.57(3) over the whole solid solution range.

Other substitutions appear to be more limited. Förtsch [14] summarized the extent of solid solution of the pyromorphite-mimetite pair in relation to vanadinite and hedyphane,  $(Pb,Cu)_3(AsO_4)_2Cl$ , from a consideration of reported analyses. The extents of the various solid solutions are shown in Fig. 11.1. Unfortunately, no

Table 11.3 — Simple zinc(II)-containing arsenate minerals found together in oxidized ores from Tsumeb [39,43]

Koritnigite	$ZnHAsO_4 \cdot 11_2O$
O'danielite	$Nu(Zn,Mg)_3H_2(AsO_4)_3$
Wavikulnrite	$Zn_3(AsO_4)_2 \cdot 211_2O$
Prosperite	$CaZn_2(AsO_4)_2 \cdot ?11_2O$
Johillerite	$Nu(Mg,Zn)_3Cu(AsO_4)_3$
Helmutwinklerite	$Pb(Zn,Cu)_2(AsO_4)_2 \cdot 211_2O$
Gaitite	$Ca_2Zn(AsO_4)_2 \cdot 211_2O$
Tsumcorite	$PbZnFe(AsO_4)_2 \cdot 211_2O$
Keyite	$(Cu,Zn,Cd)_3(AsO_4)_2$
Stranskiite	$Zn_2Cu(AsO_4)_2$
Chudobaite	$(Mg,Zn)_5H_2(AsO_4)_3 \cdot 1011_2O(?)$

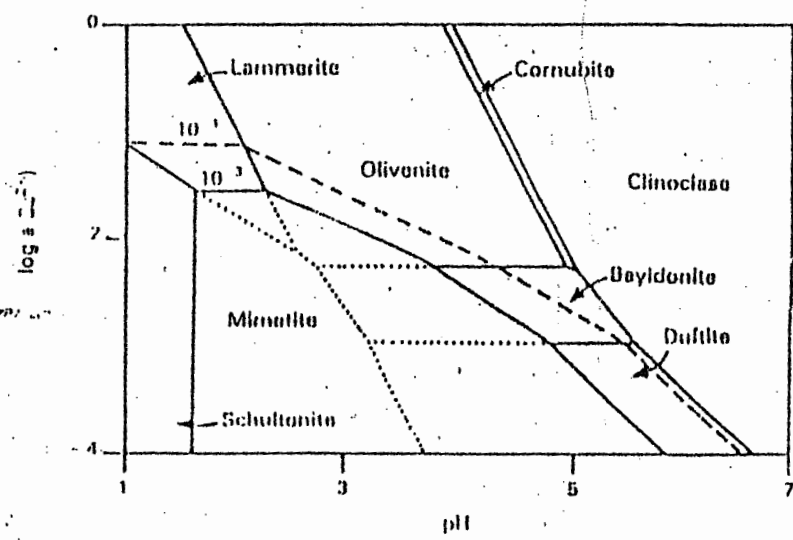


Fig. 11.7 — Regions of chemical stability for some lead arsenate minerals at 298.2K. Boundaries are calculated for a  $Pb^{2+}$  activity of  $10^{-7}$ . Fields, where they pass into that of mimetite, are shown with dotted lines. Chloride activities are indicated with respect to the mimetite field plots (see text).

defined in any equilibrium model. This can be handled with the usual calculations, but it is not necessary to develop a comprehensive set of such parameters here; indeed the complexity of the calculations in what is in effect a multidimensional phase diagram is probably only warranted for particular mineral associations from one locality. Some calculations along these lines have been reported for secondary

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amorphous and the zinc phases gave but diffuse X-ray diffraction patterns, corresponding to another synthetic layered silicate [197]. Hemimorphite has been separately synthesized in the laboratory by the latter workers.

Of considerably greater economic significance are the secondary silicate metals of uranium, which are also listed in Table 11.11. Little is known concerning their stabilities, although reliable syntheses are available for some of the species [198,199]. Stohl and Smith [198] have presented a coherent analysis of the structural aspects of this class of minerals that has been confirmed in later studies [200,201] which have also assisted in the establishment of correct stoichiometries for the various species. Some have unknown structures; oursinite, however, appears to be an analogue of uranophane [202]. Uranophane formation from primary uranium minerals in weathering granites has been discussed [203], but given the economic importance of the secondary uranium silicates it would appear that a more thorough study of the chemistry and stability of these species would be highly desirable.

Finally, it ought to be mentioned that secondary nickel silicates generated during the weathering of ultramafic and mafic rocks have long been exploited for that metal [204]. Whereas general processes of lateritization are fairly well understood, the mineral chemistry of all of the nickel-bearing phases is not. The term *garnierite* is used as a 'catch-all' for hydrous nickel silicates formed under such circumstances [2]. A number of different minerals are actually present, although not all have been recognized in all known deposits. Important phases include Ni-rich talcs and chlorites, the mineralogy of which is now well-established [205,206]. Other nickel- and cobalt-containing congeners have recently been subjected to more thorough study [207, 208].

REFERENCES

- [1] C. Palache, H. Berman, and C. Frondel, *The system of mineralogy*, 7th edn, (Wiley, New York, 1951), Vol. II.
- [2] M. Fleischer, *Glossary of mineral species*, 5th ed, (Mineralogical Record Inc., Tucson, 1987).
- [3] P. B. Moore and J. O. Nriagu, eds, *Phosphate minerals*, (Springer-Verlag, Berlin, 1984).
- [4] V. Divjakovic and W. Nowacki, *Z. Krist.*, 142, 262 (1975).
- [5] N. H. W. Sieber, E. Tillmanns, and O. Medenbach, *Amer. Mineral.*, 72, 404 (1987).
- [6] P. Phet and M. Deliens, *Bull. Mineral.*, 111, 167 (1988).
- [7] B. D. Sturman, R. C. Rouse and P. J. Dunn, *Amer. Mineral.*, 66, 843 (1981).
- [8] G. L. Shoemaker and E. Kostiner, *Amer. Mineral.*, 66, 176 (1981).
- [9] J. O. Nriagu, *Geochim. Cosmochim. Acta*, 37, 367 (1973).
- [10] A. I. Inegbuebor, J. H. Thomas, and P. A. Williams, *Mineral. Mag.*, 53, 363 (1989).
- [11] R. M. Smith and A. E. Martell, *Critical Stability Constants*, (Plenum, New York, 1976), Vol. 4.
- [12] R. A. Robie, B. S. Hemingway, and J. R. Fisher, *U.S. Geol. Surv. Bull.*, 1452, (1978).

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