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Solubility and stability of scorodite, $FeAsO_4 \cdot 2H_2O$: Reply

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INTRODUCTION

The preceding discussion by Robins (1987) presents some questions about the techniques used to obtain the solubility product of scorodite reported by Dove and Rimstidt (1985). Robins's major concern was that it was measured under conditions for which scorodite should dissolve incongruently to ferric hydroxide and aqueous arsenate. We are well aware of this problem, and we wish to emphasize that we were careful to use experimental results that showed only congruent dissolution to calculate the reported solubility product. Whereas it is true that the congruent dissolution reaction is easier to obtain at lower pH values, our experimental conditions were chosen to avoid these high ionic strength solutions for which the solubility results must be adjusted for activity coefficients and various complexes. In order to simplify the phase diagrams and the accompanying discussion, we will not distinguish the hydrolysis products of Fe and arsenate (e.g., $FeOH^{2+}$, $HAsO_4^{2-}$, etc.) but we will refer to them collectively as $Fe^{3+}_{(aq)}$ and $AsO^{3-}_{4(aq)}$. The distribution of these species can be calculated from the total concentrations of $Fe^{3+}_{(aq)}$ and $AsO^{3-}_{4(aq)}$ and the hydrolysis constants reported in Dove and Rimstidt (1985), or from ones derived from the free-energy values listed by Robins (1987).

PHASE RELATIONS

The problems of incongruent solubility of scorodite cannot be understood without a careful analysis of the phase relations involved. Figure 1, adapted from the preceding discussion, shows two invariant points, one at high pH (~4.8) and one at low pH (~0.2). The invariant point at high pH is the result of the intersection of three univariant reactions: (1) the congruent dissolution of scorodite to $Fe^{3+}_{(aq)}$ and $AsO^{3-}_{4(aq)}$; (2) the incongruent dissolution of scorodite to $Fe(OH)_{3(s)}$ and $AsO^{3-}_{4(aq)}$; (3) the congruent dissolution of $Fe(OH)_{3(s)}$. The position of this invariant point is determined by the solubility of metastable $Fe(OH)_{3(s)}$. $Fe(OH)_{3(s)}$ solubility is a function of particle size and degree of hydration (see Murray, 1979, for a review of this subject); the smaller the particles, the less stable (i.e., the more soluble) the phase. Robins has chosen probably the least-stable possible form to locate the invariant point at pH 4.8. Our experiments were done at higher pH values where, as Robins states, it is quite clear that scorodite should dissolve incongruently. The rationale for choosing such conditions is given below. However, once $Fe(OH)_{3(s)}$ forms, the particles grow, recrystallize, and eventually dehydrate to FeOOH as the metastable $Fe(OH)_{3(s)}$ gives way to ever more stable forms. As soluble ferric hydroxides with decreasing solubilities are formed, the $Fe(OH)_{3(s)}$ solubility curve (Reaction 3), and its intersection with the congruent solubility curve to form the invariant point, moves to lower and lower pH. Given enough time, $Fe(OH)_{3(s)}$ will convert to the thermodynamically stable FeOOH so that the invariant point for the three reactions under true equilibrium conditions lies at about pH = 0.2. According to this argument, if only thermodynamically stable phases are considered at 25°C and $a_{H_2O} = 1.0$, the congruent dissolution of scorodite can only occur at pH < ~0.2. All measurements of congruent solubility at higher pH values are carried out along the metastable extension of the congruent reaction curve.

However, all is not lost. Measurement of a metastable equilibrium constant is perfectly reasonable provided the investigators are careful to isolate the correct reaction. The best example in the geological sciences is the measurement of the solubility of amorphous silica at low temperatures where it should convert to quartz. This solubility curve is the metastable extension of the glass–aqueous solution reaction that can be traced hundreds of degrees Celsius below the stable phase boundary. Because quartz does not nucleate readily, solutions can be equilibrated with amorphous silica and its solubility determined. The free energy of formation of amorphous silica at low temperatures can then be calculated from the solubility data and the free energy of water and $H_4SiO_{4(aq)}$.

We did observe incongruent dissolution of scorodite in most experiments (Fig. 2), and we agree that we did our experiments under conditions for which scorodite should break down to $Fe(OH)_{3(s)}$ and $AsO^{3-}_{4(aq)}$. However, in four of these experiments we managed to assemble systems so clean that iron hydroxides failed to nucleate. Thus, scorodite was constrained to dissolve by a simple, congruent reaction as demonstrated by the equal (within analytical uncertainties) concentrations of dissolved Fe and arsenate. Note that if the reaction were incongruent because $Fe(OH)_{3(s)}$ precipitated from solution, the $Fe^{3+}_{(aq)}$ concentrations should fall appreciably below the $Fe^{3+}_{(aq)}$ values defined by the congruent dissolution line in Figure 2. The scatter of the $AsO^{3-}_{4(aq)}$ values above the congruent solubility line reflects the difficulty of measuring such low arsenate concentrations. Robins's solubility experiments were also successful because iron hydroxides failed to form in his experiments, even though they should be present according to Figure 1. The iron hydroxides that should

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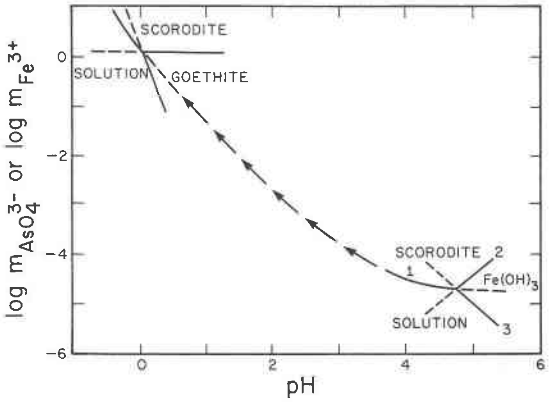

Fig. 1. Concentration verus pH (phase) diagram showing an invariant point at about pH 4.8 produced by the intersection of three univariant reactions: (1) the congruent dissolution of scorodite to $Fe^{3+}_{(aq)}$ and $AsO^{3-}_{4(aq)}$, (2) the incongruent dissolution of scorodite to $Fe(OH)_{3(s)}$ and $AsO^{3-}_{4(aq)}$, and (3) the congruent dissolution of $Fe(OH)_{3(s)}$. This form of $Fe(OH)_{3(s)}$ is very fine grained and metastable; given some time, the particles will recrystallize to form larger and less-hydrated ones that have a lower solubility. This will cause the intersection of Reaction 3 for $Fe(OH)_{3(s)}$ solubility and Reaction 1 for congruent scorodite dissolution (i.e., the invariant point) to move to the left on the diagram along the path traced by the arrows. Eventually the iron hydroxides will give way to goethite, which is the thermodynamically stable form under these conditions, so the invariant point for true thermodynamic equilibrium lies at about pH = 0.2. The boundary for the congruent dissolution of scorodite to the right of this point (arrows) is a metastable extension.

form by the incongruent dissolution reaction under the conditions of his experiments would have a relatively large particle size, and they would be unlikely to grow during the short times needed to measure the congruent solubility. Thus, even though all of these congruent solubility experiments were done on a metastable reaction, we see no reason why these solubility data should not be used to determine the thermodynamic stability of scorodite.

We wish to apologize for any misunderstanding that might have arisen from our description of the synthetic scorodite used in our experiments. Whereas we did report its color as a light tan, its color matches N9.5 to 9.7 or "very near white" on the Munsell Standard Guide of Color (1929). No iron hydroxide contamination of our experimental material was evident from the color, X-ray diffraction pattern, or microscopic examination.

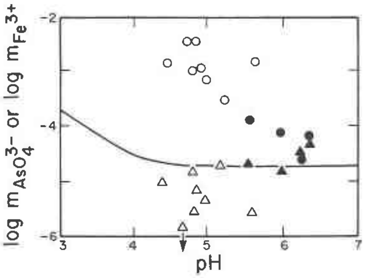

Fig. 2. Results of experiments measuring scorodite solubility starting with synthetic scorodite and pure water (from Dove, 1984). The circles represent arsenate concentrations and the triangles represent Fe^{3+} concentrations. The open symbols represent data that we believe were influenced by the incongruent dissolution reaction. The differences between the Fe and arsenate concentrations are all greater than 10^{-4} *m* (molal; see Fig. 2, Dove and Rimstidt, 1985). The filled symbols represent reactions that we believe are controlled by congruent dissolution. The line represents the approximate position of the metastable extension of the congruent solubility curve according to Robins (1986). Note that the Fe concentrations fall nearly on the congruent dissolution curve for scorodite, not significantly below it as they would if $Fe(OH)_{3(s)}$ were precipitating. The differences between the Fe and arsenate concentrations are all less than 10^{-4} *m* (see Fig. 2, Dove and Rimstidt, 1985).

COMPLEXES

One of the most difficult problems in extracting thermodynamic data for substances from solubility measurements is the extrapolation of real solution properties to the reference state of infinite dilution. This process requires a knowledge of the activity coefficients for all species and equilibrium constants for *all* aqueous complexes. The higher the concentration of the solution, the more difficult accounting for these effects becomes. Errors in estimating these values are additive and degrade the accuracy of the reported solubility product, sometimes by orders of magnitude. We chose the route of measuring scorodite solubility in nearly pure water to avoid accumulation of such errors. The calculated activity coefficients for all species in our experiments were greater than 0.99, and the amount of complexed Fe and As was less than 3.5% of the total amounts present (based on the stability of the complexes listed in Table 2 of Robins, 1986). Other than accounting for the hydrolysis of $Fe^{3+}_{(aq)}$ and $AsO^{3-}_{4(aq)}$, no adjustment of our measured concentra-

TABLE 1. Calculated activities of each $FeAsO_4$ complex in the experiments used to determine scorodite K_{sp}

Exp. no.	Reported pK_{sp}	Final pH	Total pAs (*m*)	Total pFe (*m*)	$pa_{FeHAsO_4^+}$	$pa_{FeH_2AsO_4^{2+}}$
1	21.88	5.97	4.15	4.84	6.36	9.20
2	21.71	6.36	4.27	4.32	6.58	12.06
3	22.14	6.23	4.61	4.50	6.68	12.22
4	21.31	5.53	3.86	4.69	5.31	9.96

Note: The "p" notation signifies "−log."

TABLE 2. Reported scorodite solubility products

Source	log K_{sp}
Chukhlantsev (1956)	−20.24
Nashimura and Tozawa (1978)*	−21.1
Dove and Rimstidt (1985)†	−21.7 ± 0.5
Robins (1986)‡	−22.3

* From one experiment.
† From four experiments.
‡ From reported ΔG^0_f.

TABLE 3. Selected localities where arsenopyrite and scorodite have been reported to coexist (from Dove, 1984)

Locality (and reference)	Associated minerals
Brinton mine, Floyd Co., Virginia (1)	pyrite, chalcopyrite, quartz
Gold Hill, Toole Co., Utah (2)	
Kazakhstan steppe (3)	galena
Kiura mine, Japan (4)	quartz, vivianite, fluorite
Monte Cristo, Washington (5)	
Ojeula mine, Mexico (6)	pyrite, galena
Putnam Co., New York (7)	pyrite

Note: None of these report the coexistence of loellingite, realgar, orpiment, and pyrrhotite with arsenopyrite and scorodite. References are (1) Dove and Rimstidt (1985), (2) Foshag et al. (1930), (3) Chukrov (1951), (4) Ito and Shiga (1932), (5) Spurr (1901), (6) Foshag (1937), (7) Martens (1924).

tions is required to calculate the solubility product of scorodite. Thus the reported uncertainty (precision) of our scorodite solubility product arises from the analytical uncertainties inherent in the Fe and As concentration measurements. We feel that the uncertainties of the hydrolysis constants would combine to give no more than about ±0.2 log units of uncertainty in the accuracy. Thus we sacrificed the analytical precision attainable at low pH conditions, where $Fe^{3+}_{(aq)}$ and $AsO^{3-}_{4(aq)}$ concentrations are higher and thus easier to determine, for what we feel is improved accuracy. The approach used by Robins requires that the amount of Fe and arsenate tied up in aqueous complexes (including complexes involving the supporting electrolyte as well as Fe with arsenate) be subtracted from the measured concentration of each. Errors in the formation constants of these complexes (often as large as one-half an order of magnitude), or the neglect on one or more complexing reactions, usually accumulate to an unacceptably large total. Because Robins gives no error brackets for his values, we can only speculate that the total uncertainty (accuracy) of his results is at least as large as the analytical uncertainty (precision) of ours.

RESULTS

Considering all the problems discussed here (complexes, incongruent dissolution, activity coefficients, stability of iron hydroxides), it is clear that measuring the solubility of scorodite is a difficult task. Remarkably, the agreement among three of the four published values of the solubility is very good (Table 1). This agreement is not fortuitous, as contended by Robins, but rather, it shows that we all measured the equilibrium constant for the same (metastable) congruent reaction. We agree with Robins that Chukhlantsev's (1956) value is too high, but we still believe that if it were influenced by incongruent dissolution, the Fe values should be lower, if iron hydroxides were precipitating. Therefore the solubility product calculated assuming congruent reaction would be too low, not too high, as it would be if there were a particle-size effect. In any case, a choice of a log $K_{sp} = -21.7 \pm 0.6$ for the congruent dissolution of scorodite includes all of the other reported values in Table 1.

ARSENOPYRITE OXIDATION

We agree with Robins that the oxidation of arsenopyrite is undoubtedly a very complex chemical process. However, we did not observe any orpiment, realgar, pyrrhotite, or loellingite in a reflected-light microscope examination of samples from the Brinton arsenic mine (Dove, unpub.). The pyrite in these samples appeared as macrocrystalline grains and was apparently formed by the hydrothermal solutions that precipitated the arsenopyrite. In addition, a cursory search of the literature for descriptions of other deposits in which arsenopyrite is apparently oxidizing and scorodite is present (Table 2) turned up no cases of reported association of orpiment, realgar, pyrrhotite, or loellingite with the arsenopyrite and scorodite. Although these minerals may appear in nature, as well as on calculated stability diagrams, as possible intermediates in the oxidation reaction, their absence in these examples suggests that they are difficult to nucleate or slow to grow. Our observations *did* show an intimate association of scorodite and arsenopyrite, and we call upon this evidence to suggest that arsenopyrite can oxidize directly to scorodite according to the reaction given in Dove and Rimstidt (1985).

CONCLUSIONS

Science would be a boring occupation, indeed, if we all dealt with research problems in an identical fashion. The preceding discussion by Robins illustrates his style of dealing with solubility measurements, whereas this reply illustrates the approach that we prefer in determining scorodite solubility. Both approaches are thermodynamically valid although we feel that ours produces the more accurate results. Regardless of the technique used, the reported solubility products of scorodite agree well enough to be useful for solving a variety of geological and technological problems.

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