

SOLUBILITIES OF NATURAL AND SYNTHETIC FERRIMOLYBDITE

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ABSTRACT

The uncompleted solubility curve for natural ferrimolybdate by Vinogradov (1957) was completed with good correlation for both natural ferrimolybdate and a synthetic product with identical x -ray diffraction pattern. An area of lowest solubility for natural ferrimolybdate was established at approximately 3.35 pH. This value was slightly more basic for synthetic material. The synthetic material was also less soluble throughout the whole pH range. An area immediately to the more basic side of the least solubility point was complicated by a possible iron-molybdenum complexing. In the low pH range, both natural and synthetic material showed apparent complete solubility below 1.3 final pH.

INTRODUCTION

A knowledge of the behavior of molybdenum relative to the reaction of secondary minerals and molybdenum complexes under varying conditions of depositional environment and transport is important to the geochemical prospecting of molybdenum-bearing deposits. It was with this in mind that the present study was undertaken.

The solubility of natural ferrimolybdate is at a distinct minimum between approximately pH 3 and 5. Vinogradov (1957) plotted the general outline of the solubility vs. pH curve for natural ferrimolybdate and found it to dip rather sharply to a minimum between 3.2 pH and 4.7 pH (Fig. 1). He considered the left branch of the graph to show the solubility of ferrimolybdate in acid solution and the right branch to characterize the decomposition of ferrimolybdate with precipitation of ferric hydroxide. He thought that these branches would intersect between the initial pH values of 3.2 and 4.7 and that this intersection point would correspond to the minimum solubility of ferrimolybdate. A 1.7 initial pH was the lowest run pH value that he attempted. Lack of natural material prevented his curve from being completed.

An attempt was made in this study to furnish the precise point between pH 3. and 5. which represents minimum solubility and to determine the point of complete solubility in the low pH range. Exploration in the area above 5. pH was not attempted.

METHODS AND RESULTS

Investigators who have studied natural ferrimolybdate have commented upon the paucity of materials, or have recognized contaminants such as goethite, jarosite or possibly iron-molybdenum complexes in their samples. The present study was faced with similar problems. Because of

this, the natural material was hand selected, magnetically cleaned, and acid washed before it was used in experimentation. Later, synthetic material, giving the pattern for natural ferrimolybdate, was used as a check on the results obtained from experimentation with natural material.

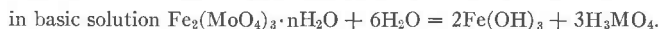
Analysis was by the thioglycolic acid colorimetric method (Snell and Snell) for both molybdenum and iron. Mo and Fe were determined simultaneously by adjusting pH of the complex formed. 0.1 g of crystalline, hand selected, and acid washed natural ferrimolybdate was placed in 250 ml of a dilute sulphuric acid solution adjusted to proper pH and allowed to reach solubility equilibrium. It was noted that, as in Vinogradov's

TABLE 1. pH AND CONCENTRATION VALUES FOR NATURAL (URAD) FERRIMOLYBDITE

Initial pH	2.50	2.95	3.25	3.50	3.75	4.0	4.25
Final pH	—	3.0	3.35	3.55	3.69	3.84	3.97
Mo (g/l)	3.74×10^{-2}	1.52×10^{-2}	9.12×10^{-3}	1.27×10^{-2}	1.07×10^{-2}	1.16×10^{-2}	1.24×10^{-2}
Fe (g/l)	1.55×10^{-2}	4.34×10^{-3}	2.17×10^{-3}	3.02×10^{-2}	2.15×10^{-2}	1.84×10^{-2}	1.65×10^{-2}

(Averaged over two runs.)

work for separate runs, the pH increased on the acid side of the minimum solubility point of the curve and decreased on the basic side (Fig. 1). That is, the mineral hydrolyzed to cause the pH of the solution in which it was immersed to shift toward the pH at the minimum point from either side. The results of this study vary slightly from the expected pH shift, and, since this range of pH deviation is small, it may be in part due to mechanical limitations of the pH meter used. Thus, it was found that a more usable curve was yielded by plotting initial pH's instead of the final ones. Final pH values were, however, used in the assessment of the minimum solubility point. The hydrolysis just discussed may proceed as follows:



Titley (1963) noted a similar occurrence when he added ferrimolybdate to neutral water. With constant stirring the pH of the solution shifted to 5. pH where it remained. He considered this reaction to be the result of "abrasion pH" which is a reflection of the surface properties of the small sized particles into which the mineral breaks on stirring.

It was found from the values of two separate series of runs, which were later averaged to construct a curve, that a definite minimum point represented by a smooth curve did not exist between the 3 and 5 pH values. Instead, as the point of least solubility was approached and passed from the acid end of the curve, a sharp rise in solubility occurred before the curve returned to its normal position (Fig. 1). This sudden rise in solu-

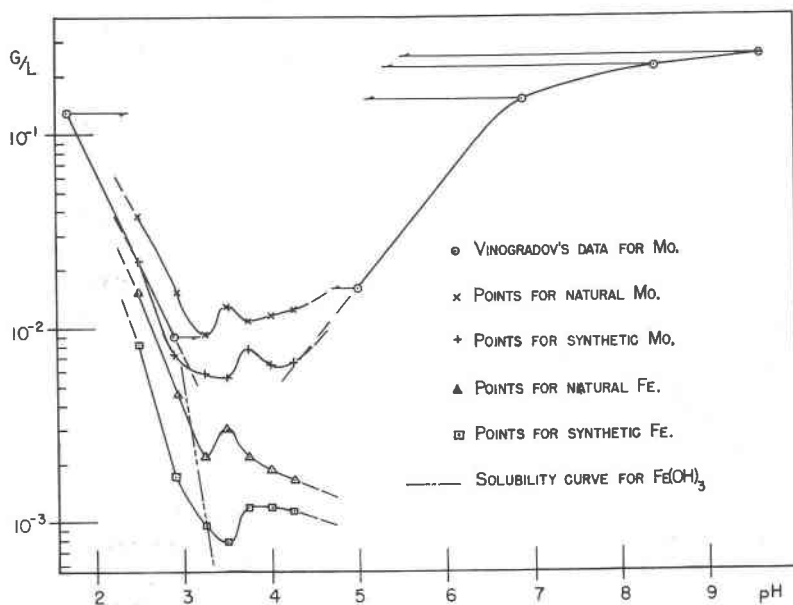


FIG. 1. Solubility of natural and synthetic ferrimolybdate as a function of the pH of the initial solution. Fe and Mo content are shown on a logarithmic scale. Arrows indicate end pH in Vinogradov's work.

bility near the minimum solubility point may be explained by the formation of a basic salt $FeOHMoO_4$, or by some iron-molybdenum complex. Formation of the basic salt is mentioned as a possibility by Nekrasov (1954). Such salt, which would hydrolyze more slowly to $Fe(OH)_3$ and which is more soluble than $Fe(OH)_3$, is also supported by the fact that the Fe concentration is higher on the basic side of the curve than can be expected by the solubility of $Fe(OH)_3$ (Fig. 1). At a pH of 4.0, $Fe(OH)_3$ would give an iron concentration of 5.58×10^{-6} g/l, whereas, the present curve shows 1.84×10^{-3} g/l. This is a much greater solubility than can be accounted for by the slight pH shift of the solution. As might be predicted, the solubility curve of $Fe(OH)_3$ crossed the experimental iron solubility curve at very nearly the minimum (Fig. 1).

After a sufficiently large amount of synthetic ferrimolybdate had been prepared, it was used in the above procedure to determine behavior and also as a possible check on the results for the natural material.

The minimum solubility for the synthetic material occurred at nearly the same pH value as that for the natural material but it was not quite as soluble throughout the whole pH range. It coincided more closely to the experimental curve of Vinogradov than to the curve of the natural material of this study (Fig. 1 and Table 2). Since the minimum solubility of

the synthetic material shifted somewhat to the basic area, and though the natural material was thoroughly cleaned, it is possible that this shift might represent either an iron contaminant in the natural material, such as goethite or absorbed iron oxide, or possibly a formula compositional difference.

The same sharp rise and fall in the solubility curve occurred on the basic side of the minimum solubility point for synthetic material as oc-

TABLE 2. pH AND CONCENTRATION VALUES FOR SYNTHETIC FERRIMOLYBDITE

Initial pH	2.50	2.90	3.25	3.50	3.75	4.00	4.25
Final pH	—	2.80	3.25	3.60	3.80	3.90	4.10
Mo (g/l)	2.12×10^{-2}	7.15×10^{-3}	5.79×10^{-3}	5.57×10^{-3}	7.72×10^{-3}	6.43×10^{-3}	6.57×10^{-3}
Fe (g/l)	8.09×10^{-3}	1.70×10^{-3}	9.57×10^{-4}	7.82×10^{-4}	1.17×10^{-3}	1.17×10^{-3}	1.13×10^{-3}

curred for natural ferrimolybdate (Fig. 1). High correlation occurred between the natural and synthetic material in this respect.

Because varying ratios of iron to molybdenum for the natural ferrimolybdate formula, such as 1.00 Fe_2O_3 to 3.09 MoO_3 (Guild, 1907) to that of 1.00 Fe_2O_3 to 3.90 MoO_3 (Simpson 1926), have been reported in the literature, an attempt was made to establish the Fe/Mo ratio in solutions for both natural and synthetic material in the low acid area of the graph. These attempts were generally unsuccessful. It was not determined whether a substitution series could be produced artificially or whether such a series in fact actually exists in natural material. Further work on this phase of the study is in progress.

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