AN EXPERIMENTAL STUDY OF THE SOLUBILITY AND SPECIATION OF MoO₃(s) IN HYDROTHERMAL FLUIDS AT TEMPERATURES UP TO 350°C—A REPLY

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To the Editor: In our paper entitled "An Experimental Study of the Solubility and Speciation of $MoO_3(s)$ in Hydrothermal Fluids at Temperatures up to 350°C," we reported results of a study designed to determine the solubility of $MoO_3(s)$ in NaCl-bearing aqueous fluids at elevated temperature. We did so in order to gain insights into the manner in which Mo is transported in the saline fluids that form porphyry Mo and Cu-Mo ore deposits. Related objectives were to identify the dominant aqueous Mo species and retrieve thermodynamic data for these species. The results of this study show that $NaHMoO_4^0$ is the dominant Mo species in NaCl-bearing fluids, except at unusually low Na^+ activity, in which $HMoO_4^-$ is the dominant species. This leads to the conclusion that Mo transport in porphyry systems is strongly favored by high salinity, high temperature (and high oxygen fugacity). To test this conclusion, we used the thermodynamic data presented in our paper to predict Mo concentrations in a hypothetical ore fluid and found that the modeled concentrations are remarkably similar to those reported by Audétat (2015) for fluid inclusions trapped under the same conditions in the Climax porphyry Mo deposit. We are therefore confident that the data presented in Shang et al. (2020) are robust and can be used reliably to model Mo transport and deposition in ore-forming hydrothermal systems.

In his "Discussion," Plyasunov (2020) does not discuss the scientific findings reported in Shang et al. (2020), which are summarized above, but instead focuses on a small set of experiments that were used to anchor this study to previous experimental studies of Mo speciation in sodium-free aqueous fluids. Moreover, Plyasunov (2020) misrepresents Shang et al. (2020) by claiming that the results of the experiments they presented are not compared to relevant results in the literature. This claim is inaccurate as should be evident to anyone reading the section in Shang et al. (2020), entitled "Comparison to previous studies." In this section and elsewhere, we discuss all relevant studies that were known to us, including those of Ivanova et al. (1975) and Dadze et al. (2017). Plyasunov (2020) identified these two papers as being particularly pertinent, despite the fact that they report results of experiments conducted in pure water and NaCl-free solutions. As we make clear above and in Shang et al. (2020), our study was carried out in NaCl-bearing aqueous fluids with the express purpose of trying to understand the behavior of Mo in fluids of the type that form porphyry Mo and Cu-Mo deposits. The papers of Ivanova et al. (1975) and Dadze et al. (2017) were therefore not immediately relevant to our study. To our knowledge, only Kudrin (1989) has reported thermodynamic data for species other than molybdic acid and its dissociation products. He reported stability constants for $NaHMoO_4^0$, the species that

we concluded is dominant in aqueous fluids with NaCl concentrations $>\sim 0.02$ *m* at temperatures above 250°C (Shang et al., 2020). In figure 6 of Shang et al. (2020), we compare the formation constants for $NaHMoO_4^0$ determined from the results of our experiments with those derived from Kudrin (1989) and show that the agreement between the two studies is excellent.

Although, for the reasons given above, most of our experiments were conducted with aqueous fluids containing significant concentrations of NaCl or sodium triflate ($NaCF_3SO_3$), we conducted a small number of experiments with solutions containing ≤0.01 m Na^+ at low but variable pH. Plyasunov (2020) has chosen to compare the results of these experiments directly to those of Ivanova et al. (1975), which were conducted in pure water and those of Dadze et al. (2017), which were conducted in pure water, 0.0001 *m* HCl, and 0.00011 *m* $HClO_4$ solutions, i.e., solutions approximating the composition of pure water. This comparison, however, is not valid—firstly, because even in a solution containing 0.01 *m* Na^+, the activity of $NaHMoO_4^0$ is significant (Shang et al., 2020), and secondly, because it ignores the other dissolved species, $H_2MoO_4^0$, $HMoO_4^-$, and MoO_4^{2-}, the concentrations of which vary with both temperature and pH (Minubayeva and Seward, 2010). Because the solubility $MoO_3(s)$ is dependent on the Mo speciation and, in turn, pH, figure 1 of Plyasunov (2020) is misleading.

In order to provide a more meaningful comparison of our data to those of Ivanova et al. (1975) and Dadze et al. (2017), we show the solubility of $MoO_3(s)$ from the three studies for 250°, 300°, and 350°C (the temperatures at which we conducted our experiments) as a function of pH(T), the pH at the temperature of the experiments (Fig. 1). For further comparison, Figure 1 also illustrates the solubility of $MoO_3(s)$ calculated from the thermodynamic data reported in the experimental study of Minubayeva and Seward (2010) on molybdic acid ionization under hydrothermal conditions and from the thermodynamic data of Shock et al. (1997) for $HMoO_4^-$ and MoO_4^{2-}. Although Shock et al. (1997) did not report thermodynamic data for $H_2MoO_4^0$, the contribution of this species to the solubility of $MoO_3(s)$ at the temperatures considered is negligible (Minubayeva and Seward, 2010) and was ignored. From Figure 1, it is evident that the solubility of $MoO_3(s)$ increases with increasing pH (and temperature), which is to be expected, given that the dominant dissolution reaction, $MoO_3(s) + H_2O = HMoO_4^- + H^+$, produces hydrogen ions and is therefore promoted by increasing pH. It is also evident that the solubility determined by Shang et al. (2020) for $MoO_3(s)$ is similar to that calculated using the data of Shock et al. (1997) and to that for the 250°C data of Minubayeva and Seward (2010); the data of Minubayeva and Seward (2010) for 300°C predict a solubility that is half an order of magnitude higher. In contrast,
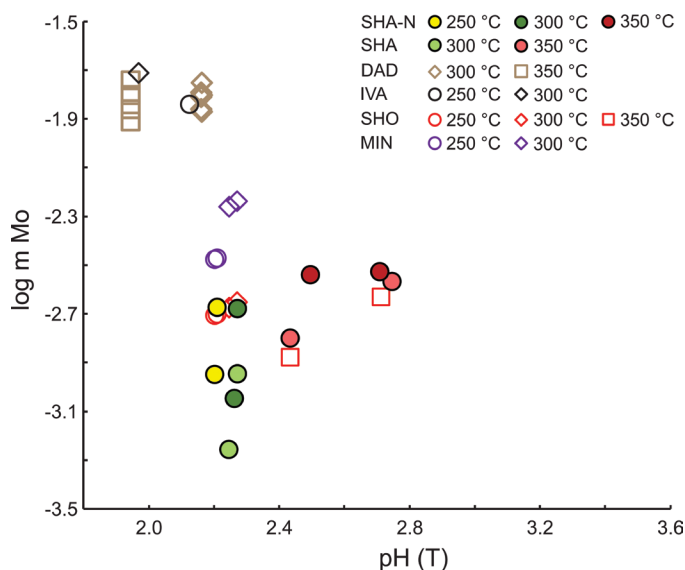
Fig. 1. A plot comparing the solubility of MoO₃(s) determined by Shang et al. (2020) at 250°, 300°, and 350°C and saturated vapor pressure as a function of pH(T) with that determined in previous studies or calculated from thermodynamic data presented in these studies. The solubility reported by Ivanova et al. (1975) was recalculated to molality to be consistent with Dadze et al. (2017) and Shang et al. (2020). As the comparison is for saturated vapor pressure, we limited the solubility data reported by Dadze et al. (2017) to that determined from experiments for 10 MPa at 300°C and 20 MPa at 350°C, i.e., pressures that are close to saturated vapor pressure. Values for pH(T) attributed to Ivanova et al. (1975), Dadze et al. (2017), and Shang et al. (2020) were calculated from the initial pH measured at ambient temperature for the corresponding experiments. The data sources referred to in the legend are as follows: DAD = Dadze et al. (2017), IVA = Ivanova et al. (1975), MIN = Minubayeva and Seward (2010), SHA = Shang et al. (2020), SHA-N = Shang et al. (2020), with 0.01 m NaCl, SHO = Shock et al. (1997).

hindsight, we should not have attempted to extrapolate our high-temperature experimental data to 25°C, given the small size of the dataset applicable to this reaction. Thus, even if the equilibrium constant reported for 25°C overestimated the true value, the good agreement between the high temperature solubility of MoO₃(s) reported in Shang et al. (2020) and that calculated using the data of Shock et al. (1997) and Minubayeva and Seward (2010), and its consistency with the predicted increase in solubility with increasing pH, provide confidence that the data from our low sodium experiments are reliable.

In closing, we remind readers that the study of Shang et al. (2020) was designed to investigate the solubility of Mo in saline hydrothermal fluids with the purpose of better understanding the genesis of economic Mo deposits. The overarching conclusion of this study was that the dominant Mo species in such fluids is $NaHMoO_4^0$. Given the importance of this conclusion for the interpretation of Mo transport and deposition in ore-forming hydrothermal systems, however, and the division of published opinion over the reasons for the higher solubility of Mo in NaCl-H₂O fluids compared to pure water (summarized in Shang et al., 2020), it needs to be corroborated by other experimental studies. It is our hope that these studies will lead to the consensus on the speciation of Mo in saline hydrothermal fluids that is needed to promote quantitative modeling of molybdenum ore genesis.

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the solubility determined by Dadze et al. (2017) and Ivanova et al. (1975) is nearly an order of magnitude higher than that determined from these studies and, contrary to the trend of increasing solubility with increasing pH identified by Shang et al. (2020), the solubility reported by Dadze et al. (2017) is independent of pH. The reason why the solubility of MoO₃(s) determined in these studies differs from that of Shang et al. (2020) and the earlier studies referred to above and why that of Dadze et al. (2017) does not increase with pH (see above) is unclear. It is also unclear why the solubility determined by Dadze et al. (2018a) for 0.1 *m* NaCl, which Plyasunov (2020) mentions as an additional basis for comparison to Shang et al. (2020), is so high.

Finally, Plyasunov (2020) has used the value reported in Table 4 of Shang et al. (2020) for the equilibrium constant of the reaction $MoO_4^{2-} + H^+ = HMoO_4^-$ at 25°C to suggest that, as this value exceeds that reported by Dadze et al. (2018b) and other studies by nearly a log unit, the high-temperature experimental data on which the estimate is based are unreliable. In