

## Research Article

# The Solubility of Tugarinovite ( $\text{MoO}_2$ ) in $\text{H}_2\text{O}$ at Elevated Temperatures and Pressures

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The solubility of tugarinovite ( $\text{MoO}_2$ ) in pure water was investigated at temperatures between 400 and 800°C and at pressures ranging between 95 and 480 MPa by using in situ synchrotron X-ray fluorescence (SXRF) to separately analyze high temperature aqueous solutions in a hydrothermal diamond anvil cell (HDAC). The concentration of molybdenum in the fluid at 400 and 500°C was below detection; however, at temperatures between 600 and 800°C, the solubility of tugarinovite increased with increasing temperature by two orders of magnitude. The molybdenum concentration at 600°C and 800°C is 44 ppm and 658 ppm, respectively. The results complement the data of Kudrin (1985) and provide the first measurement of  $\text{MoO}_2$  solubility at pressure and temperature conditions comparable to intrusion-related Mo deposit formation. The data are also relevant to the study of water chemistry and corrosion product transport in supercritical-water-cooled reactors, where Mo-bearing steel alloys interact with aqueous solutions at temperatures greater than 600°C. The application of in situ SXRF to solubility measurements of sparingly soluble minerals is recommended because it circumvents analytical uncertainties inherent in determinations obtained by quenching and weight loss measurements.

## 1. Introduction

Metal solubility data over a wide range of temperatures and pressures are fundamental for a quantitative modelling of the metal transport by hydrothermal fluids in the Earth crust and in various industrial processes. Molybdenum in magmatic ore deposits is transported and deposited by high temperature aqueous fluids exsolved from a cooling magma. Although the solubility of  $\text{MoO}_3$  (molybdite) has been experimentally investigated over a wide range of P-T-X conditions by many workers [1–7], comparatively few studies have examined the solubility of  $\text{MoO}_2$  (tugarinovite) [8–10]. In the absence of sulfur,  $\text{MoO}_2$ , rather than  $\text{MoO}_3$ , would be the stable oxide at the temperatures and  $f_{\text{O}_2}$  conditions typical for Mo ore formation [4, 7, 11, 12].

The addition of molybdenum as an alloying element increases the tensile strength and chemical durability of steel used in jet engines, gas turbines, and power generation reactors [13, 14]. Molybdenum-bearing high strength steel alloys are among the candidate materials considered for use

in the construction of the next generation of supercritical-water-cooled reactors (SCWR) [15, 16]. For example, the Generation-IV SCWR, which is designed to function at temperatures up to 625°C and pressures ranging from 25 to 30 MPa [15], is one of the six reactor design concepts developed to meet the need for an energy efficient advanced reactor [17]. An important challenge in the design and successful deployment of a SCWR is controlling water chemistry under conditions of high temperature and pressure [15, 18–21]. Hence, knowledge of the solubility of metal oxides produced at the steel-supercritical water interface is important for predicting corrosion and corrosion product transport within the reactor.

To this end, we present in situ synchrotron X-ray fluorescence (SXRF) analyses of supercritical aqueous fluids in equilibrium with synthetic  $\text{MoO}_2$  in a modified Bassett-type hydrothermal diamond anvil cell (for design details of a Bassett-type HDAC see [22]). In situ analysis of the fluid at high temperature and pressure was employed in order to circumvent errors inherent in ex situ methods [23–26].

Our results complement the data of Kudrin [8] by providing solubility measurements at pressures and temperatures comparable to intrusion-related Mo ore formation and at the anticipated operating temperature conditions of supercritical-water-cooled reactors.

## 2. Previous Studies on Molybdenum Oxide Solubility

Natural molybdenum oxides include molybdenite ( $\text{MoS}_2$ ) and tugarinovite ( $\text{MoO}_2$ ). Most solubility studies have been conducted on  $\text{MoO}_3$ . Ivanova et al. [1] performed dissolution experiments in Ti-autoclaves at vapour saturation pressures at temperatures between 150 and 300°C. The aqueous solutions, which were analyzed colorimetrically after quenching to room temperature, contained between 770 and 1390 ppm Mo. Gong et al. [2] used cold-seal pressure vessels to measure the solubility of  $\text{MoO}_3$  at 417°C at pressures between 29 and 150 MPa. They showed that, at the studied P-T conditions, the solution contained 3200 ppm Mo. In both of these studies, however, neither pH nor oxygen fugacity were constrained.

Ulrich and Mavrogenes [4] trapped solutions equilibrated with  $\text{MoO}_3$  in synthetic quartz-hosted fluid inclusions at pressures of 200 MPa and temperatures ranging between 500 and 800°C. The pH was buffered using a muscovite, K-feldspar, and quartz assemblage and the oxygen fugacity was constrained using a Ni/NiO or Re/ReO<sub>2</sub> buffer. Analysis of the synthetic fluid inclusions by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) shows that the molybdenum concentration in pure H<sub>2</sub>O increased with increasing temperature from 380 to 8155 ppm. X-ray absorption near-edge structure (XANES) spectra obtained from synthetic fluid inclusions at the temperature of liquid-vapour homogenization suggest that the dominant Mo species is H<sub>2</sub>MoO<sub>4</sub>.

Meredith et al. [5] used synchrotron X-ray fluorescence to measure the solubility of  $\text{MoO}_3$  in oxygenated water in a hydrothermal diamond anvil cell. The concentration of Mo in solution ranged from  $3995 \pm 13$  ppm at 400°C and 44 MPa to  $8663 \pm 59$  ppm at 500°C and 113 MPa.

Dadze et al. [6] determined the solubility of crystalline  $\text{MoO}_3$  in aqueous solutions of HClO<sub>4</sub> at 300°C and 10 MPa. They suggested that the acidity of the solution was a determining factor controlling the solubility of molybdenum trioxide under hydrothermal conditions and assumed that monomeric forms H<sub>2</sub>MoO<sub>4</sub><sup>0</sup>, HMoO<sub>4</sub><sup>-</sup>, and MoO<sub>4</sub><sup>2-</sup> are produced by the dissolution of  $\text{MoO}_3$ . Rempel et al. [3] studied the solubility of molybdenum trioxide in water vapour at 300, 320, and 360°C and 3.9–15.4 MPa. They reported Mo concentrations of 17.9, 23.5, and 28.7 ppm at 300, 320, and 360°C, respectively, and concluded that the predominant species is a monomeric hydrated complex of the form  $\text{MoO}_3 \cdot n\text{H}_2\text{O}(\text{g})$ . Hurtig and Williams-Jones [7] measured the solubility of  $\text{MoO}_3$  in HCl-bearing water vapour and vapour-like aqueous fluids having a density between 0.005 and 0.343 g/cm<sup>3</sup> at temperatures between 300 and 500°C and 1.3–42.5 MPa. They suggested that, at 400°C and 20 MPa,

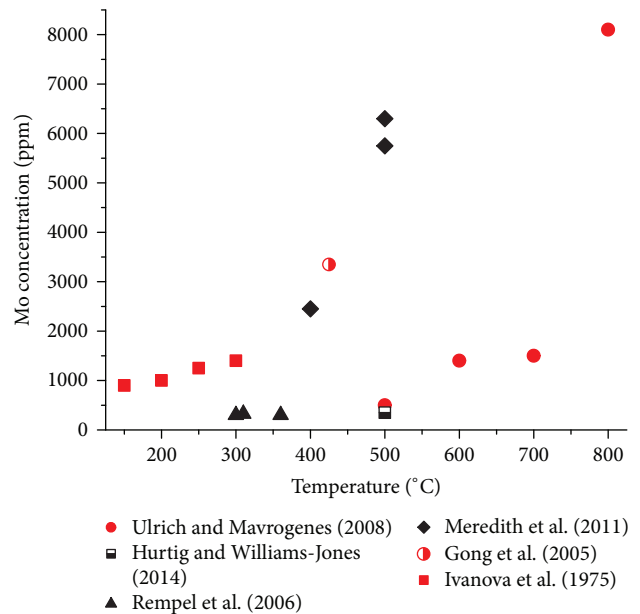


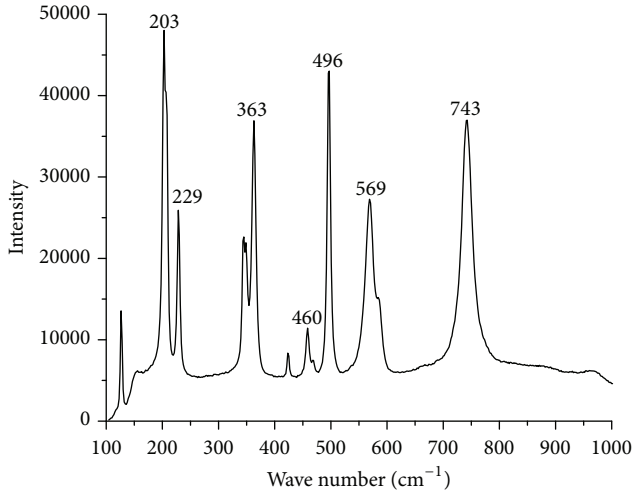
FIGURE 1:  $\text{MoO}_3$  solubility versus temperature from previous studies. Pressures reported are 44–113 MPa (Meredith et al. 2011), 200 MPa (Ulrich and Mavrogenes 2008), 29–150 MPa (Gong et al. 2005), 1.3–42.5 MPa (Hurtig and Williams-Jones 2014), and 3.9–15.4 MPa (Rempel et al. 2006). Red symbols designate  $\text{MoO}_3$  solubility in pure water.

the major molybdenum-bearing species in the low density aqueous solutions is  $\text{MoO}_3(\text{H}_2\text{O})_8$ . They also noted that the hydration number of the dominant species decreases as the temperature increases. The concentration of molybdenum in the quenched experimental condensates ranged from 3 to 481 ppm. Titanium autoclaves were used in the experiments by Rempel et al. (2006); Dadze et al. (2014) and Hurtig and Williams-Jones (2014). Figure 1 shows  $\text{MoO}_3$  solubility as a function of temperature reported in previous studies.

Comparatively few data are available on the solubility of  $\text{MoO}_2$  [8–10]. This is due to problems of measuring the solubility of sparingly soluble minerals under conditions of extreme temperature and pressure. Kudrin [8] determined the solubility of tugarinovite ( $\text{MoO}_2$ ) in water and aqueous solutions of HCl, NaOH, and KOH at temperatures between 250 and 450°C and at pressures between 9 MPa and 100 MPa. He showed that the concentration of Mo in pure water increases with increasing temperature from 0.01 ppm at 300°C to 25 ppm at 450°C. The experiments were conducted using titanium autoclaves while the redox conditions were controlled using Ni-NiO, Cu-Cu<sub>2</sub>O, or Fe<sub>3</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> buffers. Kudrin suggested that various Mo (VI) hydroxy complexes are the predominant species of molybdenum in the solution. Cao [10] studied  $\text{MoO}_2$  solubility in NaCl solution from 300 to 450°C using a chrome lined vessel and the solubility ranges from 5 to 315 ppm. He showed that, in these solutions, both Mo (V) and Mo (VI) can exist stably at high temperatures in the form of HMoO<sub>4</sub><sup>-</sup>, NaHMoO<sub>4</sub><sup>0</sup>, and Na<sub>2</sub>MoO<sub>4</sub><sup>2-</sup>.

TABLE 1: X-ray diffraction data for synthetic  $\text{MoO}_2$  crystals used as starting material and tugarinovite ( $\text{MoO}_2$ ).

Synthetic $\text{MoO}_2$ starting material				Tugarinovite (JCPDS: file number 32-671)			
Pos. [ $^{\circ}2\theta$ ]	d (Å)	Intensity	$h$	$k$	$l$	d (Å)	Intensity
18.3801	4.827	2.05	$\bar{1}$	0	1	4.805	2
25.9998	3.427	100	$\bar{1}$	1	1	3.420	100
31.9055	2.805	0.84	1	0	1	2.813	4
36.7193	2.447	7.93	2	0	0	2.442	30
			1	1	1	2.437	30
36.9918	2.430	18.92	$\bar{2}$	1	1	2.426	70
37.3586	2.407	12.09	$\bar{2}$	0	2	2.403	35
41.3568	2.183	1.67	2	1	0	2.181	6
			0	2	1	2.171	2
41.8854	2.157	2.53	$\bar{2}$	1	2	2.156	5
49.5028	1.841	2.97	$\bar{3}$	0	1	1.841	11
53.0658	1.726	11.45	2	1	1	1.725	30

FIGURE 2: Raman spectrum of synthetic  $\text{MoO}_2$  used as starting material.

### 3. Experimental Procedures

**3.1. Synthesis and Characterization of Starting Materials.** Crystals of synthetic  $\text{MoO}_2$  were grown by chemical transport using  $\text{TeCl}_4$  as a transport agent at the Institute of Physics, Augsburg University, Germany [27, 28]. X-ray powder diffraction data collected from the starting material using  $\text{CuK}\alpha$  radiation is compared to tugarinovite [29] in Table 1.

Raman spectra of the starting material, obtained using a Horiba Jobin-Yvon LabRam HR confocal instrument equipped with a 100 mW 532 nm Nd-YAG diode laser (Topica Photonics) and a Synapse charge-coupled device (CCD; Horiba Jobin-Yvon) detector at St. Mary's University, Halifax, are shown in Figure 2. Frequency calibration was performed using a pure silica standard ( $521\text{ cm}^{-1}$ ). Each Raman spectrum represents an average of two accumulations with 20-second acquisition times at 100% laser power. Raman shifts

for synthetic material are in close agreement with previously published Raman spectra obtained from  $\text{MoO}_2$  [11, 12, 30–32].

**3.2. Hydrothermal Diamond Anvil Cell.** A Bassett-type hydrothermal diamond anvil cell (HDAC) was modified so that an aqueous fluid in equilibrium with  $\text{MoO}_2$  could be separately analyzed by microbeam synchrotron X-ray fluorescence. The sample chamber consisted of a cylindrical-shaped laser-milled recess in the culet face of the upper diamond anvil and the hole in a rhenium gasket that was pressed between the two diamond anvils (Figure 3). Optical profilometer measurements indicated that the recess in the diamond is  $300\ \mu\text{m}$  in diameter and  $37\ \mu\text{m}$  deep (Figure 4), and the hole in the rhenium gasket is  $125\ \mu\text{m}$  deep and  $400\ \mu\text{m}$  in diameter.

The diamond anvils were fitted into silicon nitride seats located at the center of two opposing stainless steel platens. The platens were then drawn together along three guide posts using tightening screws. Each silicon nitride seat was heated using platinum resistance wire while the temperature of the system was monitored using S-type (Platinum-Rhodium) thermocouples (Omega™) and controlled with a programmable temperature controller. The temperature of sample chamber was calibrated by observing the melting point of  $\text{NaNO}_3$  ( $308^\circ\text{C}$ ), the alpha-beta phase transition of quartz ( $573^\circ\text{C}$ ), and the melting point of  $\text{NaCl}$  ( $801^\circ\text{C}$ ). The water density was determined from the observed liquid-vapour homogenization temperature and the pressure at a given temperature was calculated using the equation of state (EOS) of water [33–35]. The EOS of pure water is a good estimate of pressure because of the very low Mo concentration in the fluid at all temperatures and pressures measured.

The  $\text{MoO}_2$  crystal resides on the culet face of the lower diamond anvil and within the Re gasket (Figure 3(a)). A horizontal X-ray microbeam passes through the fluid-filled recess in the diamond anvil above the Re gasket. This configuration ensures that the incident X-ray beam does

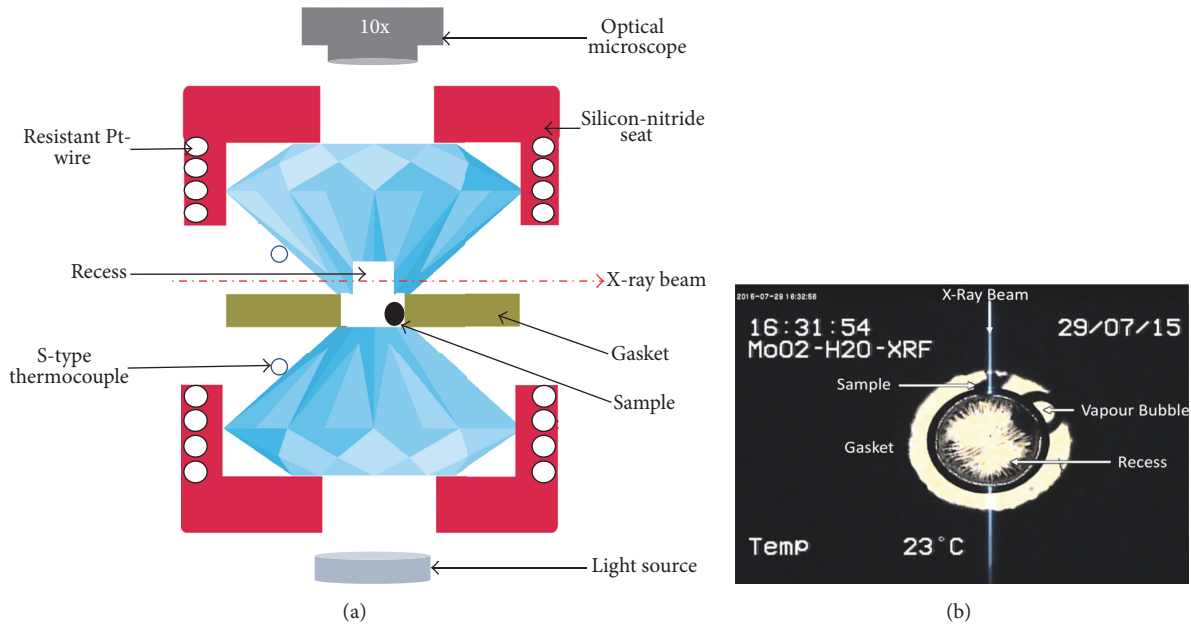


FIGURE 3: (a) The schematic diagram of the modified hydrothermal diamond anvil cell. The upper diamond anvil was recessed and the X-ray beam went through the recess. A rhenium gasket was squeezed by two diamond anvils together. A 10x objective microscope was placed on top of the HDAC to view the sample chamber in real time. (b) shows the sample chamber at room temperature. The  $\text{MoO}_2$  sample, vapour bubble, and the recess of the upper diamond are visible. The sample chamber is surrounded by the rhenium gasket. The X-ray beam path (blue line) is also visible.

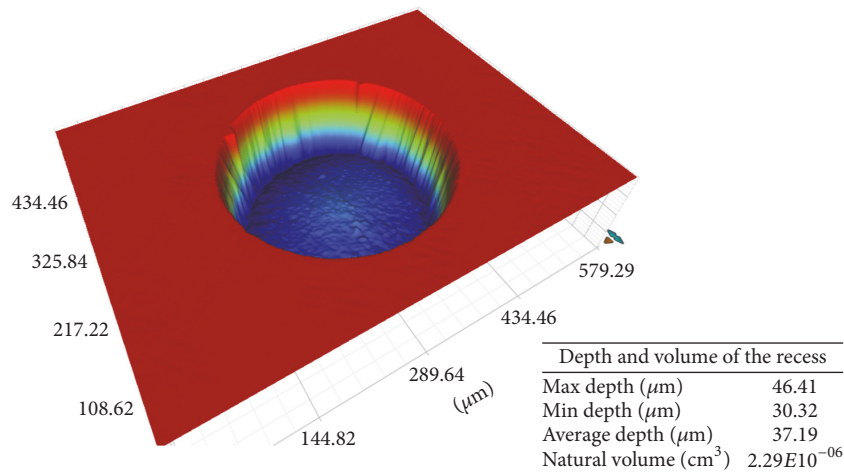


FIGURE 4: 3D profile of the culet face of the recessed diamond anvil. Inset shows the depth and volume of the recess. This 3D profile was prepared using an optical profilometer.

not interact with the  $\text{MoO}_2$  crystal and that the detector is shielded from possible excitation of the crystal by scattered X-rays. Figure 3(b) is a photograph of the sample chamber as viewed through the diamond anvils showing the vapour bubble, the opaque  $\text{MoO}_2$  crystal fragment in  $\text{H}_2\text{O}$ , and the path of the X-ray beam through the sample chamber.

The HDAC was purged with argon gas in order to prevent oxidation at high temperatures. Kapton film windows on the wall of the HDAC allowed for transmission of the incident beam and the exit of fluorescence X-rays from the sample to the detector.

The redox conditions of the system at various temperatures were buffered by the reaction  $\text{Re} + \text{O}_2 \leftrightarrow \text{ReO}_2$  [36–39]. The appearance of rhenium oxide on the gasket surface indicates that partial oxidation of the Re metal gasket occurred in these experiments (Figure 5).

**3.3. Synchrotron X-Ray Fluorescence Analysis.** Synchrotron X-ray fluorescence (SXRF) spectra were collected using the X-ray microprobe at beamline 20-ID at the Advanced Photon Source (APS), Argonne National Laboratory. X-ray fluorescence spectra were collected using a four-element Vortex



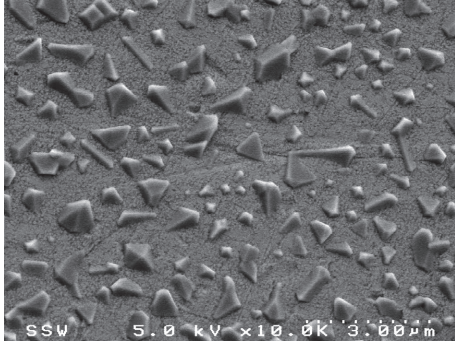


FIGURE 5: SEM image of  $\text{ReO}_2$  crystals on the rhenium gasket surface after following the experiment.

TABLE 2: Measured Mo concentrations in standard solutions.

Standard (ppm)	Measured concentration (ppm)
10	31
50	75
100	141
500	543
1000	977
2500	2500

detector positioned horizontally at  $90^\circ$  to the incident X-ray beam. The energy of the incident X-rays was 23.2 keV and the beam flux was  $1 \times 10^{11}$  photons/second. The precise positioning of the X-ray beam through the sample chamber was facilitated by the visible fluorescence of the beam in the diamond anvil (Figure 3(b)).

Standard solutions having Mo concentrations of 10, 50, 100, 500, 1000, and 2500 ppm were used to derive a calibration curve. The solutions were prepared by diluting 10000 ppm (GFS Chemical) or 1000 ppm (Fluka Analytical) stock solutions with deionized water. An average of seven spectra was collected from each standard solution in the HDAC. The integration time for each spectrum was 60 s. PyMCA spectral analysis software [40] was used to analyze all SXRF spectra.

Table 2 gives the measured Mo concentrations for the standard solutions and Figure 6 shows the calibration curve determined by linear regression of the standard solution data [41].

**3.4. Experimental Method.** Deionized water, a small fragment of synthetic  $\text{MoO}_2$ , and an air bubble were sealed in the sample chamber in the HDAC (Figure 7(a)). The gasket was conditioned by repeated heating and cooling until the observed liquid-vapour homogenization temperature ( $T_H$ ) was constant.

Spectra were collected from the fluid in 30-minute intervals for up to 4 hours. The HDAC was held at 400, 500, 600, 700, and 800°C for at least 30 minutes before the first spectrum was collected.

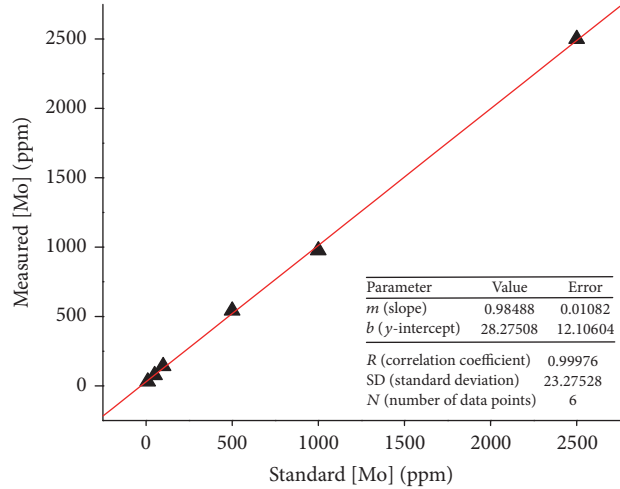


FIGURE 6: Calibration curve derived from measured Mo concentrations in standard solution.

TABLE 3: The measured concentration of Mo in solution at different temperatures and pressures.

Temperature ( $^\circ\text{C}$ )	Pressure (MPa)	Concentration (ppm)
400	95	bdl*
500	193	bdl*
600	292	44 ( $\pm 26$ )
700	387	67 ( $\pm 26$ )
700	387	117 ( $\pm 26$ )
800	479	658 ( $\pm 43$ )

\*bdl: below detection limit.

It was noted during trial runs that prolonged exposure to the X-ray beam at high temperatures resulted in the precipitation of a Mo-rich solid from the fluid at some point along the beam path (Figure 7(b)). In order to eliminate this effect, spectrum acquisition was limited to 60 s intervals.

Two-dimensional Mo  $K\alpha$  elemental maps of the sample chamber were made at each pressure and temperature condition to correct for any changes in the position of the HDAC due to thermal expansion and to make sure that no Mo-bearing solids, formed by beam-induced radiolysis, were present.

## 4. Data Treatment and Results

The density of the fluid ( $684 \text{ kg/m}^3$ ) was calculated from the observed liquid-vapour homogenization temperature ( $313^\circ\text{C}$ ). Table 3 gives the pressure and temperature condition for each SXRF measurement.

The concentration of dissolved Mo in the fluid at each temperature and pressure condition was determined using the linear regression parameters of the calibration curve (Table 3). Examples of SXRF spectra obtained for three different molybdenum standards are shown in Figure 8. The

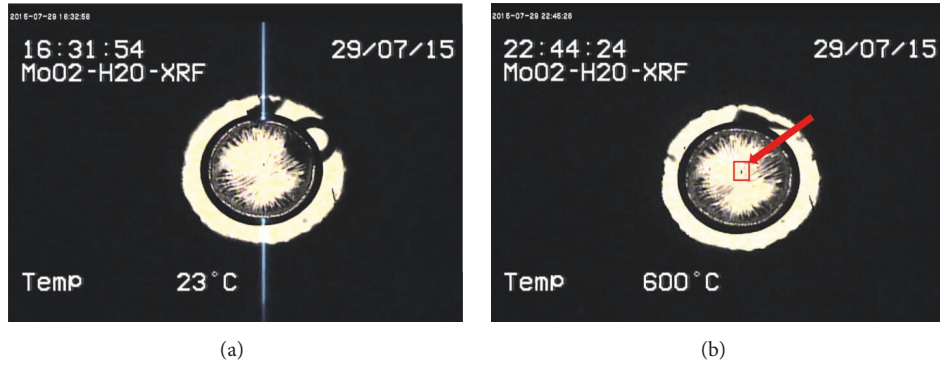


FIGURE 7: View of the sample chamber in the HDAC at 23°C (a) and 600°C (b). Note the presence of a vapour bubble at room temperature and a small opaque phase (red arrow) in the center of sample chamber at 600°C.

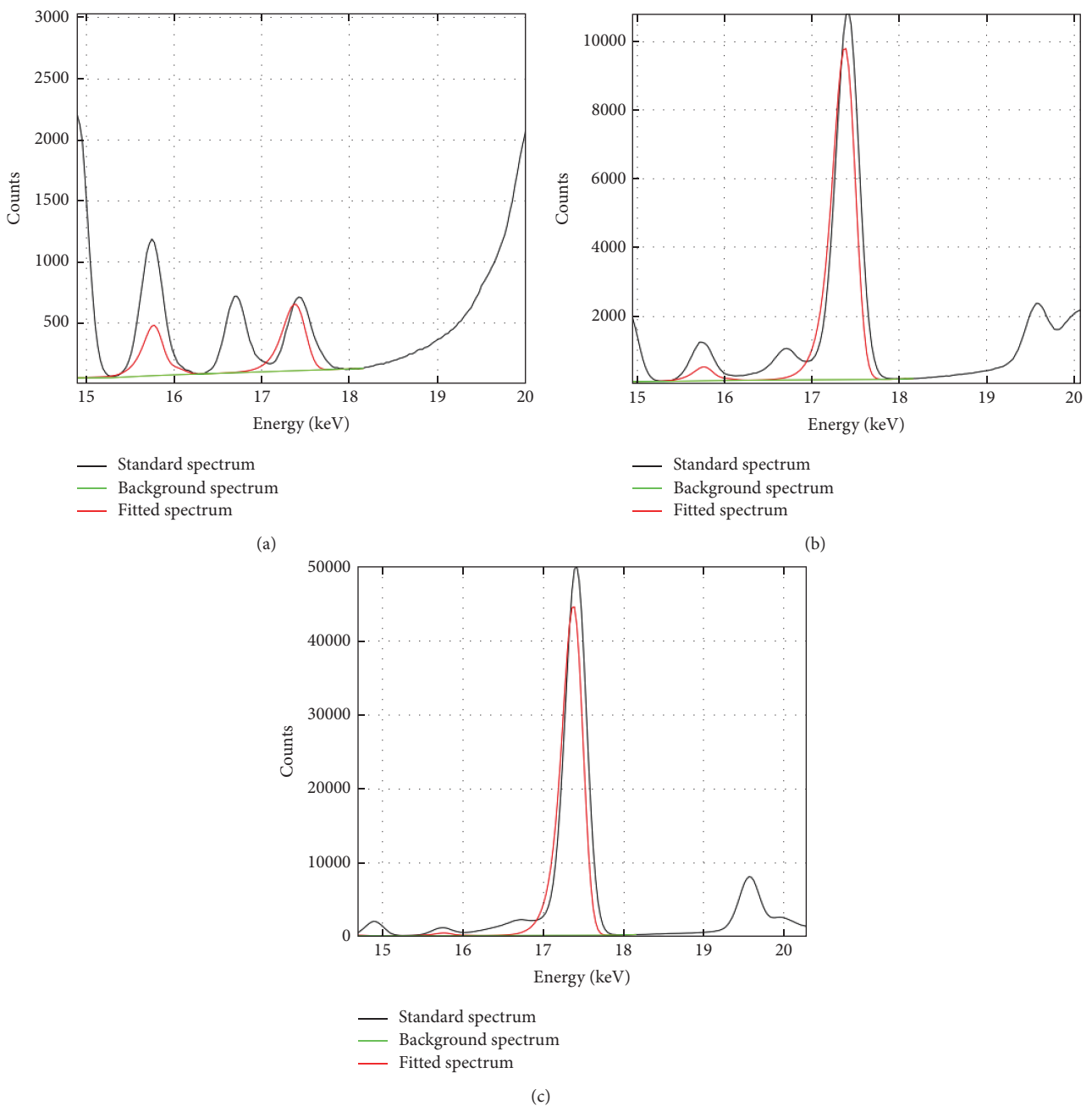


FIGURE 8: X-ray fluorescence spectra obtained from Mo standards (a) 10 ppm, (b) 500 ppm, and (c) 2500 ppm.

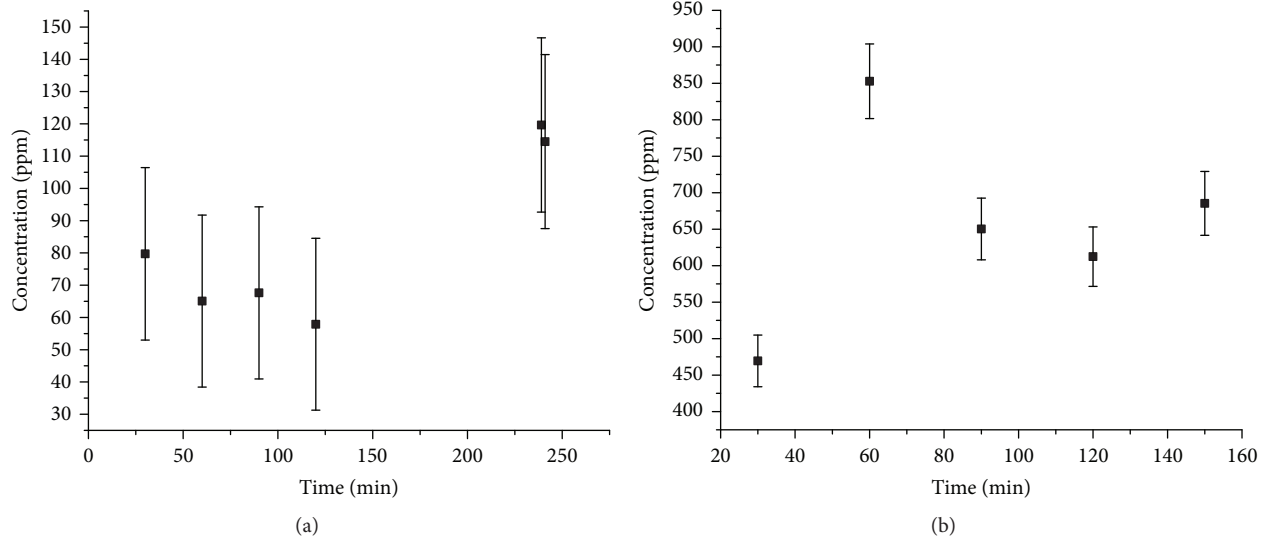


FIGURE 9: Variation of Mo concentration determined from XRF spectra collected at different time intervals at (a) 700°C and (b) 800°C.

uncertainty of the measured concentration was calculated using

$$S_x = \frac{S_y}{|m|} \sqrt{\frac{1}{k} + \frac{S_m^2 x^2}{S_y^2} + \left(\frac{S_b}{S_y}\right)^2 - \frac{2xS_m \bar{x}}{S_y^2}}, \quad (1)$$

where  $S_x$  is the uncertainty in  $x$ ,  $|m|$  is the absolute value of the slope,  $S_y$  is the standard deviation of the measured values of  $y$ ,  $b$  is the intercept value,  $S_b$  is the intercept error or the estimate of standard deviation of the intercept,  $S_m$  is the slope error or the estimate of standard deviation of the slope,  $\bar{x}$  is the arithmetic mean of used standard concentrations, and  $k$  is the number of replicate measurements of the unknown [41].

A minimum detection limit (MDL) of 0.5 to 3.0 ppm Mo was calculated from  $3c\sqrt{I_b}/I_p$ , where  $c$  is the standard concentration,  $I_b$  is the background intensity, and  $I_p$  is the peak intensity [42, 43].

Kudrin [8] examined the dissolution kinetics for  $\text{MoO}_2$  in pure water and showed that equilibrium was attained after about 2 hours at 450°C and  $\log f_{\text{O}_2} = -25.1$ . The HDAC in our study was held between 2 and 4 hours prior to SXRF analysis. Figure 9 shows that at 700°C the Mo concentration varies from  $70 \pm 26$  ppm in the first 2 hours and increases to  $117 \pm 27$  ppm after four hours. At 800°C, the Mo concentration is 686 ( $\pm 43$ ) ppm after 2.5 hours.

## 5. Discussion

Previous studies have shown that the molybdenum oxide solubility is effected to different degrees by solution composition, temperature, pressure, pH, and oxygen fugacity. Our analyses show that there is an exponential increase in solubility at temperatures above 500°C (Figure 10) which indicates that pure water could transport significant concentrations of Mo at magmatic temperatures.

Ulrich and Mavrogenes [4] presented solubility data for molybdenum in  $\text{H}_2\text{O}$  at temperatures between 500 and

800°C. In all of their experiments  $\text{MoO}_3$  was reduced to  $\text{MoO}_2$  and Mo was oxidized to  $\text{MoO}_2$ . The presence of a small opaque phase, interpreted to be  $\text{MoO}_2$ , present in some of their synthetic fluid inclusions indicates that  $\text{MoO}_2$  precipitated from the solution at high temperatures prior to microcrack healing. If equilibrium was attained before fluid entrapment, then the concentration of Mo in that fluid should reflect the solubility of  $\text{MoO}_2$ . However, the solubility reported by Ulrich and Mavrogenes (2008) at 800°C and 200 MPa (i.e., 0.8 wt%) is more than an order of magnitude higher than the solubility reported in the present study. This discrepancy may be due in part to differences in the pressure conditions used in the different experiments or because the synthetic inclusions represent samples of fluid that equilibrated with the highly soluble  $\text{MoO}_3$  used as starting material in the experiments of Ulrich and Mavrogenes (2008). The reduction of the fluid at high temperatures may have resulted in the precipitation of  $\text{MoO}_2$  during closure and necking of the fluid-filled microcracks in quartz.

*5.1. Molybdenum in Intrusion-Related Hydrothermal Systems.* Many ore deposits of molybdenum form in high temperature intrusion-related hydrothermal systems. Fluid inclusion studies suggest that Mo deposition usually occurs at temperatures between 450 and about 700°C and pressures between 100 and 170 MPa [44–51]. Furthermore, Mo is thought to be transported by low to intermediate density, supercritical aqueous fluids [52–56] as mononuclear hydroxy complexes [57–61]. Although Mo is usually transported in the hexavalent state it is also transported in a lower valence state ( $+4$ ) under more reducing conditions [8, 62].

The temperature-redox conditions for porphyry Mo deposits are shown in Figure 11 [63, 64]. At these ore-forming conditions,  $\text{MoO}_2$  rather than  $\text{MoO}_3$  is the stable oxide [4, 7, 11, 12]. Fluid inclusion studies of porphyry Mo deposits indicate that low salinity fluids play an important role in Mo transport [65–70]. Candela and Holland [58] concluded that

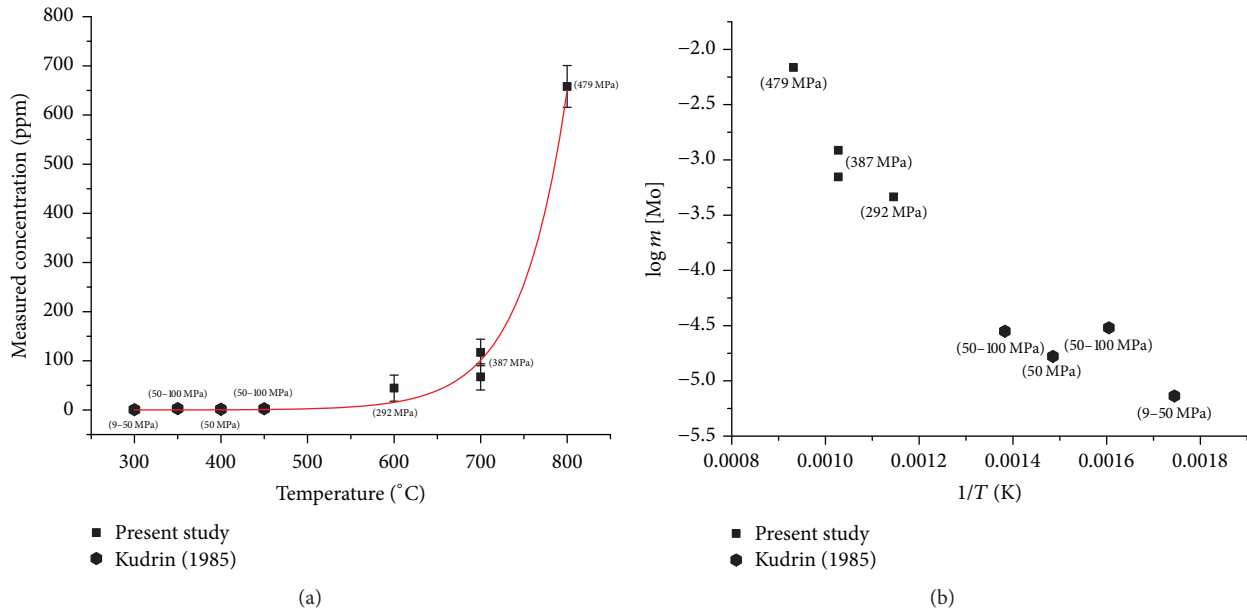


FIGURE 10: Solubility MoO<sub>2</sub> solubility in pure water as a function of temperature. The pressure condition for each measurement is shown on each plot.

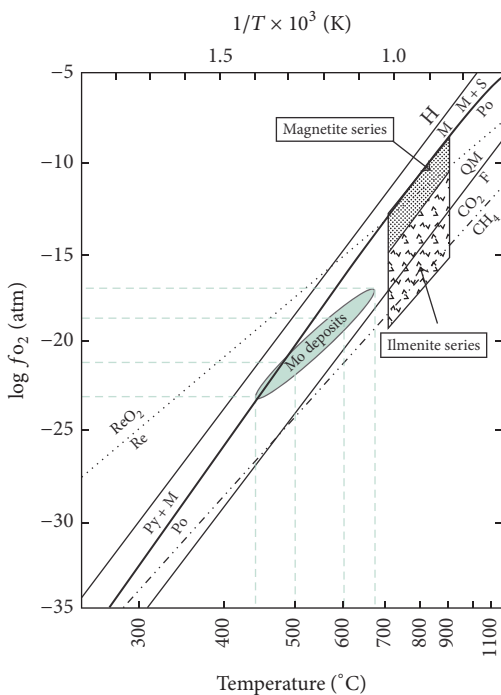


FIGURE 11: Temperature and  $f_{O_2}$  conditions for porphyry Mo deposits (modified after Ishihara et al. 2006). Re-ReO<sub>2</sub> buffer curve is shown.

in magmatic systems Mo partitioning is independent of the chlorine content of magmas and associated aqueous phases. Zajacz et al. [54] studied the effect of fluid chlorinity as a parameter on fluid/melt partitioning. They distinguished a group of elements (As, Mo, Cu, Sb, Bi, and B) displaying

a distinct negative correlation with the chlorinity of the fluid, which suggests transport as non-chloride (i.e., hydroxy) complexes. Of these elements, Mo, As, Sb, and B are known to occur as hydroxy complexes in hydrothermal fluids [71–74]. Fluorine is not an important ligand involved in the hydrothermal transport of Mo in granite-related systems [58, 61, 75]. Some studies have demonstrated the importance of chloride complexing for Mo partitioning [4, 76]. Ulrich and Mavrogenes (2008) suggested a correlation between the solubility of Mo oxides and the chloride content in the fluid. Tattitch and Blundy (2017) have shown that fluid-melt Mo partition coefficient increases with the increasing salinity and a mono-chloride complex controls Mo partitioning. The results presented here may explain why low salinity fluid inclusions prevail in some Mo ore deposits. The presence of sulfur in such systems would result in the precipitation of molybdenite [10, 77–79].

**5.2. Relevance of MoO<sub>2</sub> Solubility to Supercritical-Water-Cooled Reactor (SCWR).** As discussed above, Generation-IV SCWR is designed to function at temperatures up to 625°C and at pressures ranging from 25 to 30 MPa. The successful deployment and long term operation of these SCWR depends on the durability of the materials in the presence of water under conditions of extreme temperature, pressure, and radiation [15, 18–20]. Mo-bearing alloys are among the candidate materials considered in the construction of SCWR. Previous experiments have shown that a significant amount of Mo from the walls of Hastelloy C and Alloy 625 autoclaves may be dissolved in pure water at 450°C after 280 hours [15]. Molybdenum oxides may form in the passivation layer of steel alloys [80–87] and dissolution of these oxides could result in contamination and degradation of the reactor performance by creating thermal barriers on heat transfer surfaces.



The next generation of supercritical water reactors are expected to operate at even higher pressures and temperatures [17]. The data shown in this study indicate that partial dissolution of a Mo-bearing passivation layer in a SCWR may affect water chemistry and the efficiency of the reactor. This example underscores the need to compile a more comprehensive oxide solubility database that can be used to predict supercritical water chemistry. To achieve this goal, we recommend that in situ SXRF solubility measurements be employed to experimentally evaluate the durability of candidate alloys under conditions of extreme temperature and pressure.

## 6. Conclusions

In situ synchrotron X-ray fluorescence analysis of aqueous fluids in a modified hydrothermal diamond anvil cell was used to determine the solubility of synthetic MoO<sub>2</sub> in pure water up to 800°C and 480 MPa. The results show an exponential increase in solubility at temperatures above 600°C to a maximum concentration of 658 ± 43 ppm Mo at 800°C and 480 MPa. The results on the MoO<sub>2</sub>-H<sub>2</sub>O system provide insights into Mo transport in pure water and in low salinity, high temperature aqueous solutions involved in ore-forming systems. The data are also relevant to understanding Mo transport in supercritical-water-cooled reactors and demonstrate the potential of in situ SXRF for further solubility studies of sparingly soluble oxide minerals under conditions of extreme temperature and pressure.

## Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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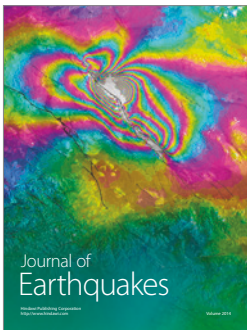
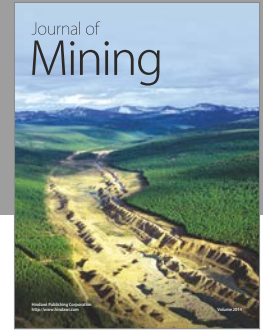
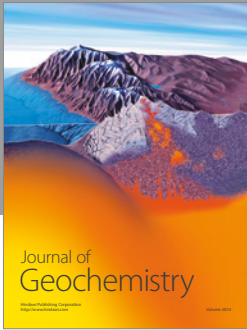
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