



RESEARCH ARTICLE

10.1002/2014EA000059

Key Points:

- Laboratory experiment on dissolution of Mo-bearing sulphides shows equal results
- O₂ concentration of ~72 ppmv is sufficient to oxidize and dissolve Mo species in water
- This value coincides with published estimates based on modeling approaches

Supporting Information:

- Figures S1 and S2 and Table S1

Correspondence to:

N. D. Greber,
greber@uchicago.edu

Citation:

Greber, N. D., U. Mäder, and T. F. Nägler (2015), Experimental dissolution of molybdenum-sulphides at low oxygen concentrations: A first-order approximation of late Archean atmospheric conditions, *Earth and Space Science*, 2, 173–180, doi:10.1002/2014EA000059.

Received 2 DEC 2014

Accepted 13 APR 2015

Accepted article online 23 APR 2015

Published online 23 MAY 2015

©2015. The Authors.

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

Experimental dissolution of molybdenum-sulphides at low oxygen concentrations: A first-order approximation of late Archean atmospheric conditions

Nicolas D. Greber^{1,2}, Urs Mäder¹, and Thomas F. Nägler¹

¹Institute of Geological Sciences, University of Bern, Bern, Switzerland, ²Now at Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois, USA

Abstract The abundance of atmospheric oxygen and its evolution through Earth's history is a highly debated topic. The earliest change of the Mo concentration and isotope composition of marine sediments are interpreted to be linked to the onset of the accumulation of free O₂ in Earth's atmosphere. The O₂ concentration needed to dissolve significant amounts of Mo in water is not yet quantified, however. We present laboratory experiments on pulverized and surface-cleaned molybdenite (MoS₂) and a hydrothermal breccia enriched in Mo-bearing sulphides using a glove box setup. Duration of an experiment was 14 days, and first signs of oxidation and subsequent dissolution of Mo compounds start to occur above an atmospheric oxygen concentration of 72 ± 20 ppmv (i.e., 2.6 to 4.6 × 10⁻⁴ present atmospheric level (PAL)). This experimentally determined value coincides with published model calculations supporting atmospheric O₂ concentrations between 1 × 10⁻⁵ to 3 × 10⁻⁴ PAL prior to the Great Oxidation Event and sets an upper limit to the molecular oxygen needed to trigger Mo accumulation and Mo isotope variations recorded in sediments. In combination with the published Mo isotope composition of the rock record, this result implies an atmospheric oxygen concentration prior to 2.76 Ga of below 72 ± 20 ppmv.

1. Introduction

The history of the earliest rise of atmospheric oxygen is a matter of considerable debate. Most data and model calculations indicate a first major increase in atmospheric O₂ during the Great Oxidation Event (GOE), a period that took place 2.5 to 2.3 Ga ago [e.g., Bekker *et al.*, 2004; Konhauser *et al.*, 2011]. During that time, O₂ increased to about 0.15 times the present atmospheric level (PAL) [e.g., Farquhar *et al.*, 2000; Holland, 2006]. This early history of the atmosphere has been inferred from several different proxy's like the occurrence of reduced detrital mineral phases such as pyrite, uraninite, and siderite in sedimentary rocks [e.g., Rasmussen and Buick, 1999; Bekker *et al.*, 2004; Johnson *et al.*, 2014], the behavior of Fe in paleosols [e.g., Rye and Holland, 1998], or mass independent fractionation (MIF) of sulphur isotopes recorded in marine sediments [Farquhar *et al.*, 2000]. Model calculations combining chemical and physical weathering of pyrite and uraninite imply an atmospheric O₂ value below 1.53 × 10⁻⁴ PAL for the time 2.42 Ga ago [Johnson *et al.*, 2014], in line with suggested O₂ levels not exceeding 1 × 10⁻⁵ PAL prior to the GOE based on the MIF of sulphur [Pavlov and Kasting, 2002].

An alternative view discussed in detail in Ohmoto *et al.* [2014] proposes an oxygenated environment with O₂ levels 50% above the PAL already before 3.5 Ga ago. However, evidence from isotope proxies of redox sensitive elements as, e.g., molybdenum, chromium, and iron suggest a more complex history of the accumulation of O₂ in the early atmosphere. The isotopic composition of Mo, Cr, and Fe in the rock record indicates an increase in free O₂ approximately 200 Ma before the GOE [Wille *et al.*, 2007; Frei *et al.*, 2009; Voegelin *et al.*, 2010; Duan *et al.*, 2010; Czaja *et al.*, 2012], in line with more recently measured sulphur isotope data from the Kidd Creek area in Ontario, Canada [Kurzweil *et al.*, 2013]. The chemical signatures of rocks from the Pongola Supergroup (South Africa) indicate that free oxygen in the atmosphere [Crowe *et al.*, 2013] or at least regionally active oxygenic photosynthesis [Planavsky *et al.*, 2014] may have existed already around 3.0 Ga ago. In contrast, the Fe isotope composition and U-Th-Pb systematic of 3.46 Ga old cherts [Li *et al.*, 2013] as well as Mo-Cr isotope compositions of 3.46 to 2.76 Ga old sediments [Wille *et al.*, 2013] from the Pilbara Craton (NW Australia) argue for an anoxic atmosphere until 2.76 Ga. Unknown is if

the inferred enhanced oxygen concentration 3.0 Ga ago of around 3×10^{-4} PAL as suggested by *Crowe et al.* [2013] persisted permanently and globally in the atmosphere. Short-term jumps in atmospheric O₂ levels [*Lyons et al.*, 2014] or regionally restricted “oxygen oases” in an otherwise anoxic environment [*Olson et al.*, 2013; *Reinhard et al.*, 2013; *Lalonde and Konhauser*, 2015] could account for the chemical signatures observed in the Pongola Supergroup.

Quantitative information about the O₂ concentration prior to the GOE is scarce and relies predominantly on model calculations. The knowledge of the sensitivity of the various proxies to the atmospheric and oceanic O₂ concentration is currently insufficient but is essential for improving the interpretation of the acquired data. Molybdenum is a redox sensitive element with several different oxidation states of which Mo^{IV} and Mo^{VI} are the most common. While solids containing reduced Mo^{IV} are insoluble in water, solids containing Mo^{VI} are readily soluble and produce molybdate oxyanions like MoO₄²⁻, HMoO₄⁻, or H₂MoO₄ [*Greim*, 2009]. For Mo concentration and Mo isotope composition to work as a proxy for the earliest rise of atmospheric oxygen relies therefore on the assumption that the change observed in the Mo signature of marine sediments is linked to the start of the accumulation of free O₂ in Earth's atmosphere and the subsequent oxidation, dissolution, and isotope fractionation of different molybdenum species in the ocean [e.g., *Anbar et al.*, 2007; *Wille et al.*, 2007; *Scott et al.*, 2008]. The relation of oxidative weathering and solubility of Mo compounds in water to atmospheric O₂ levels has not yet been quantified, however. To improve on this parameter, we conducted laboratory experiments on molybdenite (MoS₂) and on a highly Mo enriched hydrothermal breccia containing Mo-bearing sulphides using a glove box at controlled O₂ levels. Sulphide minerals like molybdenite and pyrite are the predominant recent sources of Mo to rivers [*Miller et al.*, 2011] and, even more importantly, prone to oxidative weathering. Therefore, also at the time when free O₂ started to accumulate in Earth's atmosphere, oxidation of sulphides most likely was the most important process discharging dissolved Mo^{VI} compounds to rivers and the ocean. Also, the high Mo concentrations in the two samples, i.e., molybdenite and the breccia enriched in Mo-bearing sulphides, simplify the analytical procedure and are thus well suited for the experiments performed.

2. Experiment Setup and Analytical Techniques

2.1. Samples and Sample Preparation

Two different sample types have been used for the experiments. The first is a fine molybdenite (MoS₂) powder (grain size 100 to 300 μm) produced by drilling from sample AJ008 published in *Greber et al.* [2011]. Microscope and scanning electron microscope (SEM) studies revealed that the MoS₂ is very pure and contamination or mineral intergrowth is absent. The second sample derives from the “Grimsel breccia,” a hydrothermal breccia highly enriched in Mo, located near Grimsel Pass, Switzerland. This rock was produced by mixing of oxidizing near-surface water and a reducing hydrothermal fluid, leading to the precipitation of substantial amounts of Mo, U, and sulphide minerals like pyrite and marcasite [*Hofmann et al.*, 2004]. It was not possible to identify the Mo-bearing phase with X-ray diffraction, SEM, and Raman measurements on untreated and leached powder separates. According to *Hofmann et al.* [2004], Mo-bearing sulphide minerals occur as black, submicrometric pigments that exhibit a dark-brown olive color in thin sections. Furthermore, this black pigmentation is not associated with an increased pyrite content but rather with high Mo-concentrations, and thus, pyrite is not the main host for Mo. However, observed good correlations between Fe, S, and Mo concentrations show that Mo is incorporated in a sulphide phase, either a Fe-Mo-sulphide or MoS₂ in crystalline (i.e., molybdenite) or amorphous form [*Hofmann et al.*, 2004]. The material for the experiment was taken from sample Gr28 [see *Hofmann et al.*, 2004; *Greber et al.*, 2011]. The dark, fine-grained matrix enriched in Mo (see Figure S1a in the supporting information) was separated from the quartz and feldspar clasts and subsequently milled under dry conditions (grain size 80 to 100 μm) using an agate disk mill. The chemical composition of the produced sample powder has been measured using standard XRF techniques on a powder pellet and revealed a Mo concentration of 1830 μg/g (see Table S1 in the supporting information).

Four dialysis tubes from ZelluTrans, i.e., semi permeable membrane filters, that allow dissolved Mo species to pass but not solid particles have been filled with sample material. Two of them with 45 and 57 μg of molybdenite and two with 97 and 123 μg of Grimsel breccia powders, respectively. The tubes have a nominal molecular weight cutoff of 25'000 that corresponds to an effective pore size of approximately 5 nm. After filling, the tubes were bent and closed at the top with a clip. The U-shaped lower parts of the tubes

were later hung into 100 mL polypropylene beakers (see Figures S1b and S2 in the supporting information) for conducting the experiments. The molybdenite and Grimsel breccia sample powders were washed with 0.1 M HCl and subsequently with MilliQ water in the glove box to remove oxidized surface species.

2.2. Glove Box Setup and Experiment

For the experiments, a Type A vinyl glove box and an auto airlock from Coy Laboratory Products Inc. were used. A fan was running continuously to guarantee a well-mixed atmosphere that consisted of around 97.5% N₂ and 2.5% H₂. The oxygen and hydrogen concentrations of the glove box atmosphere were measured with a Model 10 gas analyzer that was connected to an external Watlow controller device and a USB data acquisition connected to a laptop to record the oxygen concentration in the glove box continuously every 3 min. The gas analyzer is able to measure the O₂ concentration in a range from 0 to 1999 ppmv with a detection level of 1 ppmv and a full-scale error of 1%, i.e., ± 20 ppmv, independent of the atmospheric O₂ concentration. The Watlow controller could only be configured to record concentrations up to 210 ppmv (an issue of high resolution versus a large range). In one experiment, the O₂ concentration in the glove box was set above the 210 ppmv threshold and therefore was controlled and read 3 times a day manually from the analyzer. Oxygen was scavenged from the glove box atmosphere using one or two platinum scrubbers that catalyze hydrogen oxidation to H₂O. The scrubbers can be used with integrated fans that force air past the scrubbers to ensure completely anoxic conditions in the glove box if so desired. In order to establish stable and low levels of oxygen concentrations, the scrubbers were detached from the fan. This reduced the reaction rate of oxygen and hydrogen to water and allowed a stationary state to be achieved between oxygen diffusing into the glove box and oxygen scavenging. To generate different levels of oxygen, the surface area of the scrubbers exposed to the atmosphere was adjusted.

Three 2 L water bottles were stored in the glove box prior to the start of the experiments and kept with an open lid for several weeks to ensure equilibrium with respect to O₂ for the atmosphere-water system. Whenever a bottle was empty, it was refilled, put back in the glove box, and used after the other two were emptied. Hereby, the water was always able to equilibrate with the low O₂ glove box atmosphere. A ninefold vacuum purge of the airlock, refilled 8 times with pure N₂, and in the last step with high purity forming gas (8% H₂), ensured material transfer into and out of the glove box without disturbing its atmospheric composition.

Two different types of experiments were performed simultaneously in each batch with water from the same preexposed water bottle. In type 1 experiments, the sample powder was held permanently below the MilliQ water surface for 2 weeks, while in the type 2 experiments, the sample powder was exposed for 1 week to the artificial glove box atmosphere and for the second week immersed in MilliQ water. These two procedures have been applied using always the same samples under different O₂ concentrations ranging from 0 to 320 ± 30 ppmv (Table 1). A 1 week break between experiments was kept, except when the change in the atmospheric O₂ concentration was below the ± 20 ppmv full scale error of the gas analyzer. In this latter case, the experiments were accomplished continuously (e.g., E1.2 to E1.5; see Table 1). Start and end dates of each experiment are shown in Table 1.

The polypropylene beakers were filled with 80 mL of MilliQ water, of which 5 to 15 mL evaporated during the experiment. Therefore, not the final Mo concentration in the water, but the total dissolved Mo is the significant measure. During each experimental batch, a blank experiment was performed as well using the type 2 experimental procedure; i.e., an empty ZelluTrans dialyses tube was hung into a beaker and filled with 80 mL of MilliQ water that was preexposed 1 week to the glove box atmosphere. The Mo concentration measurements were done in the same way as for the normal samples. Experiments have been done in three sets between March 2013 and early 2014, with breaks of 2 and 5 weeks in between, respectively. The first set of experiments has been accomplished from March to early July, the second from mid-July until the start of September, and the third from October to January. The average daily laboratory temperature during the winter months (third set of experiments, min. 18°C) was cooler than during the summer months (first and second sets of experiments, max. 26°C).

The O₂ concentration during an experiment is presented with the median. To avoid short recorded aberrant signal spikes, the 2.5% and the 97.5% percentiles (i.e., 95% confidence interval) of the recorded O₂ concentration data in the glove box were calculated and used as error estimates. The resulting oxygen level variations were lower than the ± 20 ppmv full-scale error of the analyzer except in experiment E1.6

Table 1. Experimentally Determined Total Dissolved Mo (ng) Under Various Atmospheric Oxygen Concentrations

Date		Oxygen Concentration (ppmv)			Total Mo dissolved (ng)					
From	To	2.5% Percentile	Median	97.5% Percentile	MoS ₂ Water ^b	MoS ₂ Air ^c	Breccia Water ^b	Breccia Air ^c	Blank	
Set 1										
E1.2	12 Mar 13	25 Mar 13	0	0	0	4	12	-	-	0.07
E1.3	26 Mar 13	08 Apr 13	0	0	3	2	9	-	-	0.07
E1.4	09 Apr 13	22 Apr 13	0	2	5	3	13	-	-	0.03
E1.5	23 Apr 13	06 May 13	23	26	30	16	12	-	-	0.12
E1.6	14 May 13	27 May 13	70	91	111	18	81	-	-	0.05
E1.7	28 May 13	10 Jun 13	91	97	108	11	426	-	-	0.21
E1.8	18 Jun 13	01 Jul 13	185	196	209	17	539	-	-	0.31
Set 2										
E2.1	16 Jul 13	29 Jul 13	172	193	207	9	204	100	32	0.07
E2.2 ^a	02 Aug 14	15 Aug 13	290	320	350	8	244	179	50	0.10
E2.3	24 Aug 13	06 Sep 13	57	72	79	3	74	17	39	0.17
Set 3										
E3.2	14 Oct 13	28 Oct 13	29	48	52	5	7	2	6	0.10
E3.3	04 Nov 13	18 Nov 13	7	10	11	2	9	3	2	0.05
E3.4	26 Nov 13	02 Dec 13	89	102	117	6	27	8	3	0.03
E3.6	09 Dec 13	23 Dec 13	153	166	174	4	54	43	7	0.04
E3.7	24 Dec 13	07 Jan 14	165	188	209	4	118	39	8	0.02

^aOxygen concentration manually recorded three times per day.

^bWater: Type 1 experiment: the sample powder was constantly below the water surface.

^cAir: Type 2 experiment: the sample powder was exposed 1 week to the atmosphere and 1 week kept below the water surface.

and E3.7 and when the O₂ was manually read (E2.2; see Table 1). Conservatively, whenever the deviation between percentile and median was smaller than the full-scale error, the latter has been used for data interpretation. The median and the highest and lowest values are used for the one case where the O₂ concentrations were read manually 3 times a day.

The sampled MilliQ water was then used for isotope dilution Mo concentration measurements using a ⁹⁷Mo/¹⁰⁰Mo double spike. The water samples have been evaporated to dryness at 100°C on a hotplate and then digested in 0.5 M HNO₃ for the measurement on a Nu instruments multicollector–inductively coupled plasma–mass spectrometry. The analytical setup is described in Greber *et al.* [2012]. Adsorption of Mo species on the walls of the polypropylene beakers was tested by splitting water samples in two and adding a post experiment 1 M HCl rinse of the polypropylene beakers to one fraction. No significant differences in the resulting Mo amount were observed between the two fractions. Thus, adsorption of Mo species on the walls of the polypropylene beakers is considered insignificant.

3. Results

Atmospheric oxygen concentration in the glove box and total dissolved Mo in the sample waters are shown in Table 1. The continuous external recording of the O₂ concentration in the glove box revealed that the oxygen stayed rather constant and did not vary more than the full-scale error (i.e., ±20 ppmv) of the gas analyzer for most experiments. All water samples have higher Mo concentrations than the blank, even for experiment E1.2 measured with turned-on fans and installed platinum scrubbers to keep the O₂ level as low as possible, i.e., below the detection limit of 1 ppmv (see first set of experiments in Table 1).

The type 1 and type 2 experiments, where molybdenite was used as sample material, show different behavior with respect to the amount of mobilized Mo (see Figure 1). Water samples from type 1 experiments, where molybdenite was constantly submerged, show an almost invariable low Mo concentration independent of the oxygen concentration. In contrast, water samples from type 2 experiments, where molybdenite was exposed to the glove box atmosphere prior to immersion, reveal a positive correlation between dissolved Mo and atmospheric oxygen above an O₂ concentration of 72 ± 20 ppmv. Below this value, the total amount of dissolved Mo in the water between the type 1 and type 2 experiments was almost identical with 8 ± 3 ng (2 standard error (SE), *n* = 12; see Table 1 and Figure 1). It is interesting to note that the

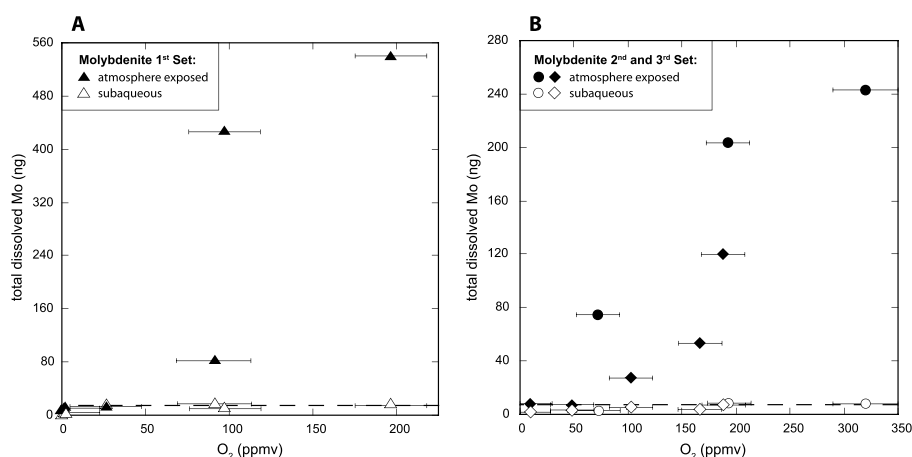


Figure 1. Results of experiments using molybdenites as substrate. (a) Data of first, (b) second, and third sets of experiments. From an oxygen concentration of 72 ± 20 ppmv, the samples exposed to the glove box atmosphere (filled symbols) start to release more Mo to the water than the samples immersed constantly in MilliQ water (empty symbols). Notice the higher Mo content in water during the first set of experiments than in subsequently following ones. The dashed lines represent the interpreted background Mo based on subaqueous samples. Errors on oxygen concentrations are the 2.5% and 97.5% percentiles or the O₂ full-scale error of the gas analyzer (i.e., ± 20 ppmv), whatever is larger.

amount of Mo dissolved in the water at a given O₂ concentration above a threshold of 72 ppmv decreases from batches 1–3. While in the first batch, 539 ng Mo got mobilized at an O₂ concentration of 196 ppmv; in the third batch, only 118 ng Mo was released at an O₂ value of around 188 ppmv.

The water samples from experiments using Grimsel breccia exhibit a different Mo signature between the type 1 and type 2 setup as well (see Figure 2). The breccia powder sample that was exposed 1 week to the atmosphere

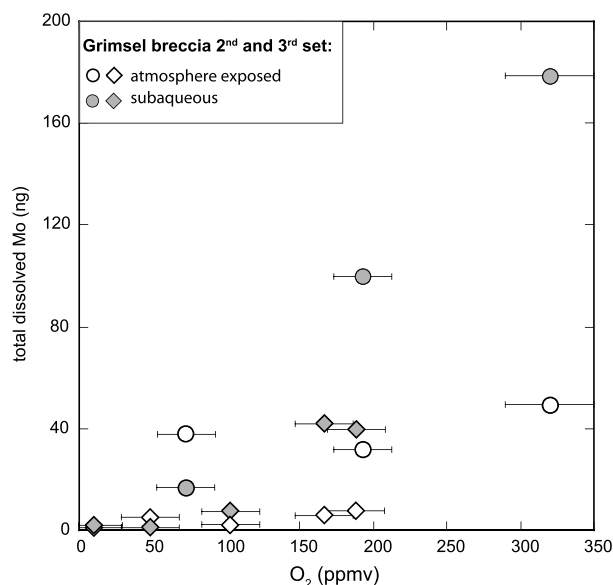


Figure 2. Results of the experiments performed with Grimsel breccia samples. The subaqueous samples (grey symbols) start to release more Mo to the water from an atmospheric oxygen concentration of 72 ± 20 ppmv. The experiments where the Grimsel breccia was exposed to the atmosphere (empty symbols) do not show any correlation with the oxygen concentration and are regarded as failed (see text). Errors on the O₂ concentration are either the 2.5% and 97.5% percentiles or the O₂ full-scale error of the gas analyzer of ± 20 ppmv, whatever is larger.

and then immersed in water liberates Mo without any obvious correlation to the oxygen concentration in the atmosphere. In this experiment, a change in color of the breccia powder from black-brown to a bright greyish-brown was observed (see Figure S3 in the supporting information). The results of the type 1 experiments show a positive correlation between the total amount of dissolved Mo in the water and the atmospheric oxygen concentration once 72 ± 20 ppmv are reached. Thus, the type 2 experiments performed with molybdenite and the type 1 experiments done with Grimsel breccia exhibit a very similar dependence between dissolved Mo and atmospheric O₂ pressure (see Figure 3).

4. Discussion

4.1. Molybdenum Dissolution at Low Atmospheric Oxygen Concentrations

In all sets of experiments using molybdenite, the sample immersed constantly in water does release a very low and almost constant amount of Mo to the water (< 18 ng; see Figure 1). The same very low Mo amounts

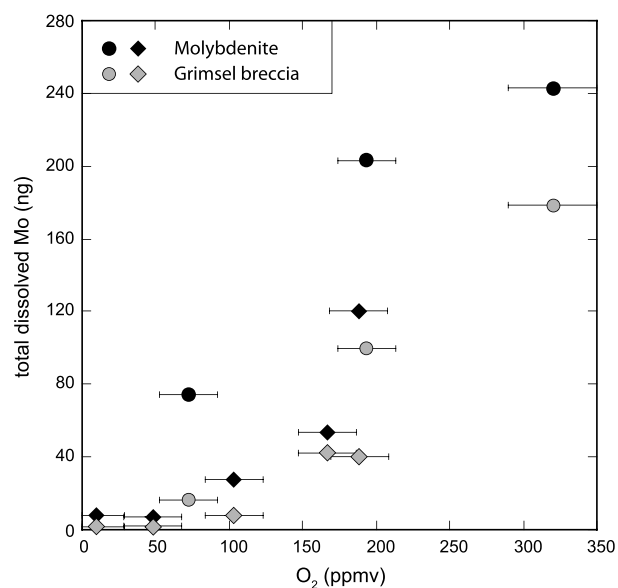


Figure 3. Comparison of the experimental produced data with molybdenite exposed to the atmosphere (black symbols) and Grimsel breccia always kept submersed (grey symbols). These two experiments show very similar patterns and indicate that with both sample materials Mo starts to become oxidized at an atmospheric O₂ concentration of 72 ± 20 ppmv. Errors on oxygen concentrations are the 2.5% and 97.5% percentiles or the O₂ full-scale error of the gas analyzer (i.e., ± 20 ppmv), whatever is larger.

molybdenite. In type 2 experiments, Mo gets oxidized on the molybdenite surface during the preexposure to the glove box atmosphere. These oxidized Mo species were subsequently dissolved once the sample had been submerged. The amount of Mo found in experimental waters below the oxygen threshold of 72 ± 20 ppmv, even under anoxic conditions of experiment E1.2, is small but significantly higher than observed in the procedural blanks. Potential explanations for this are (i) a minor additional blank source not detected in the blank measurement procedure due to sample handling, (ii) a minor Mo release that is not related to oxides, or (iii) small leftover of already oxygenated Mo surfaces on the molybdenite crystals prior to the start of the experiment. Irrespective of these possibilities, a dramatic increase of Mo release from molybdenite is observed only in type 2 experiments with oxygen levels ≥ 72 ppmv. This is a strong indication that from this threshold value on, Mo gets actively oxidized on the molybdenite surfaces, while the low Mo background prior to that value is a relict signature. The amount of Mo released to the water decreases in the experiment with molybdenite from set to set. As can be seen in Figure 1, especially in the first set, almost twice the amount of Mo gets mobilized and dissolved in water. Because always the same sample is used for all experiments, the most probable explanation is that intrinsic factors changed the dissolution rate of the molybdenite crystals. As outlined in Lüttge *et al.* [2013], changing reacting sites of a crystal due to its dissolution can lead to a nonlinear decrease in its dissolution kinetics. In addition, the first two sets of experiments were performed in summer when the average room temperature was highest. This resulted in more water evaporating and therefore of a higher humidity in the glove box atmosphere, a matter that positively influences the kinetic of the oxidation of Mo in molybdenite [Ross and Sussman, 1955].

The samples of the Grimsel breccia submersed in water from the first set of experiments are not appropriate, as they still needed to be cleaned more intensely to remove oxidized surface species. In experiments where the Grimsel breccia was exposed to the experimental atmosphere (second and third sets), the water samples show very constant Mo contents within each set (5 ± 2 and 40 ± 10 ng, 2 SE), irrespective of the ambient oxygen concentration in the glove box (see Figure 2). Thus, the first experiment (set 2) released about 8 times more Mo than the second one (set 3) at any given O₂ concentration. The sample powder also changed color during the experiment, suggesting that the mineral surfaces were strongly altered and potentially blocked further reaction progress, while the sample was exposed to the atmosphere. An

were found in the water samples of the type 2 experiments where the molybdenite was exposed 1 week to the glove box atmosphere and afterward immersed in water for another week up to an ambient atmospheric oxygen concentration of 72 ± 20 ppmv (full-scale error of gas analyzer), which equals 2.6 to 4.6×10^{-4} PAL. For higher O₂ concentrations, however, significantly more Mo was released to the water in all type 2 experiments (≥ 27 ng; see Figure 1b). Differences in the water chemistry can be excluded as reason for the distinct amount of Mo observed in the two experimental setups because type 1 and type 2 experiments were performed simultaneously with water from the same bottle. This difference using molybdenite as substrate can be explained with its strong hydrophobic nature [Zhao *et al.*, 2013] and is in line with earlier experimental results that suggest that Mo in molybdenite gets more readily oxidized when exposed to the atmosphere [Ross and Sussman, 1955]. Thus, the distinct Mo pattern between the two experimental setups is a result of the unique hydrophobic physical property of

answer as to which chemical reaction caused this clogging, and thus, the failure of the experiment cannot be presented, however. The Mo content in the water of the Grimsel breccia sample that was immersed constantly follows closely the trend observed for the molybdenite sample exposed to the atmosphere (Figure 3) and therefore supports the onset of Mo oxidation from an atmospheric oxygen concentration of 72 ± 20 ppmv.

The amounts of Mo dissolved in the water for both the molybdenite (exposed to the glove box atmosphere) and the Grimsel breccia samples (always immersed in water) are similar. This is unexpected as the quantity of Mo in the molybdenite sample is much higher, and thus, more Mo is available to get dissolved than from the Grimsel breccia samples. Therefore, it seems that the Mo in the Grimsel breccia is more reactive and easier to mobilize than in the molybdenite samples, and this is most probably related to the presence of pyrite that is abundant in the Grimsel breccia. Pyrite is suggested to have a catalytic effect on the oxidation and dissolution rate of Mo because it is a mineral with a hydrophilic nature and if it gets digested in water releases sulphuric acid that could then attack the Mo-bearing mineral.

In summary, the dramatic increase of dissolved Mo at 72 ± 20 ppmv of oxygen in the controlled glove box atmosphere is consistent with several identical subsequent experiments and with two different types of Mo-bearing substrates. This is a strong indication that at least from this threshold value of oxygen, Mo in Mo-bearing sulphides can become significantly oxidized and dissolved in water.

4.2. Implications for Atmospheric Conditions Before the Great Oxidation Event

The artificial atmosphere produced in the glove box obviously deviates from the atmosphere prior to the GOE. The composition of the atmosphere as well as the temperature during the Archean Eon is a highly disputed topic. Due to the faint young Sun paradox, the existence of a CO₂-CH₄ greenhouse gas mixture to preserve Earth from freezing [Rye *et al.*, 1995; Haqq-Misra *et al.*, 2008] is advocated. Therefore, a higher CO₂ and lower N₂ concentration as well as the suggested existence of CH₄ in the Archean atmosphere [e.g., Holland, 2006; Catling and Claire, 2005; Zerkle *et al.*, 2012] are the most evident differences to our glove box setup. The CO₂ concentration in the Archean atmosphere (≥ 0.03 atm [e.g., Haqq-Misra *et al.*, 2008]) was substantially higher than in our glove box (≤ 0.03 atm), and thus, the pH of Archean waters could have been lower than in our experiments. A more acid regime and more time for chemical reactions are factors that are assumed to lower the needed O₂ concentration for the oxidation of Mo. Therefore, the experimentally determined value of 72 ± 20 ppmv (i.e., 2.6 to 4.6×10^{-4} PAL) is a maximum value needed to oxidize and subsequently mobilize molybdenum. The inferred O₂ threshold value based on our experimental setup therefore sets an upper limit to the molybdenum isotope and element proxy for past ocean and atmosphere oxygenation to work.

Modeled pre-GOE oxygen concentration of the atmosphere range from 1×10^{-5} to 3×10^{-4} PAL [Pavlov and Kasting, 2002; Crowe *et al.*, 2013; Johnson *et al.*, 2014]. Thus, published estimates based on modeling approaches, and the experimentally determined value presented in this study coincide closely.

5. Conclusions

Using an experimental glove box setup, it has been demonstrated that it is possible to oxidize reduced Mo in sulphide minerals and to liberate and subsequently dissolve it in water at and above an atmospheric O₂ concentration of 72 ± 20 ppmv. A preoxidation of molybdenite surfaces at a low O₂ atmosphere is required to liberate Mo, and this can be explained with the unique hydrophobic physical nature of molybdenite. Mo-bearing sulphides associated with pyrite do not require to be exposed to the atmosphere prior to dissolution in water likely due to the associated acidification. The coincidence of the presented results with published model calculations and the Mo isotope composition of the rock record implies an atmospheric oxygen concentration prior to 2.76 Ga of below 72 ± 20 ppmv (i.e., 2.6 to 4.6×10^{-4} PAL).

The experimental setup does not reflect a priori natural environmental conditions, but the results can be used as first-order comparison to existing terrestrial weathering interfaces like, e.g., bare rock surfaces in mountain ranges (type 1 experiment) or stony riverbeds and lakeshores (type 2 experiment). However, benthic and soil environments have been lately advocated to be the most likely environment for first local oxidative weathering of redox sensitive elements [see Lalonde and Konhauser, 2015]. Therefore, experimental setups that more closely reflect various environmental conditions are needed to further elucidate the required atmospheric O₂ concentration to mobilize molybdenum.

Acknowledgments

This project was supported by SNF grant 126759 to T.F.N. Data were obtained according to explanation in the section *Experiment Setup and Analytical Techniques*. The corresponding author (greber@uchicago.edu) of the manuscript can be asked for raw data of isotope dilution Mo concentration measurements and oxygen concentration monitoring of the glove box atmosphere. Timothy Lyons and two unknown reviewers are acknowledged for their constructive criticism, and Jonathan Jiang is thanked for the editorial handling.

References

- Anbar, A. D., et al. (2007), A whiff of oxygen before the Great Oxidation Event?, *Science*, 317(5846), 1903–1906.
- Bekker, A., H. D. Holland, P.-L. Wang, D. Rumble, H. J. Stein, J. Hannah, L. L. Coetzee, and N. J. Beukes (2004), Dating the rise of atmospheric oxygen, *Nature*, 427(6970), 117–120.
- Catling, D. C., and M. W. Claire (2005), How Earth's atmosphere evolved to an oxic state: A status report, *Earth Planet. Sci. Lett.*, 237, 1–20.
- Crowe, S. A., L. N. Døssing, N. J. Beukes, M. Bau, S. J. Kruger, R. Frei, and D. E. Canfield (2013), Atmospheric oxygenation three billion years ago, *Nature*, 501(7468), 535–538.
- Czaja, A. D., C. M. Johnson, E. E. Roden, B. L. Beard, A. R. Voegelin, T. F. Nägler, N. J. Beukes, and M. Wille (2012), Evidence for free oxygen in the Neoproterozoic ocean based on coupled iron-molybdenum isotope fractionation, *Geochim. Cosmochim. Acta*, 86, 118–137.
- Duan, Y., A. D. Anbar, G. L. Arnold, T. W. Lyons, G. W. Gordon, and B. Kendall (2010), Molybdenum isotope evidence for mild environmental oxygenation before the Great Oxidation Event, *Geochim. Cosmochim. Acta*, 74(23), 6655–6668.
- Farquhar, J., H. Bao, and M. H. Thieme (2000), Atmospheric influence of Earth's earliest sulfur cycle, *Science*, 289, 756.
- Frei, R., C. Gaucher, S. W. Poulton, and D. E. Canfield (2009), Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes, *Nature*, 461(7261), 250–253.
- Greber, N. D., B. A. Hofmann, A. R. Voegelin, I. M. Villa, and T. F. Nägler (2011), Mo isotope composition in Mo-rich high- and low-T hydrothermal systems from the Swiss Alps, *Geochim. Cosmochim. Acta*, 75(21), 6600–6609.
- Greber, N. D., C. Siebert, T. F. Nägler, and T. Pettke (2012), $\delta^{98/95}\text{Mo}$ values and molybdenum concentration data for NIST SRM 610, 612 and 3134: Towards a common protocol for reporting Mo data, *Geostand. Geoanal. Res.*, 36(3), 291–302.
- Greim H. (2009), *The MAK-Collection for Occupational Health and Safety*, 1st ed., edited by H. Greim, Wiley-VCH, Hoboken, N. J.
- Haqq-Misra, J. D., S. D. Domagal-Goldman, P. J. Kasting, and J. F. Kasting (2008), A revised, hazy methane greenhouse for the Archean Earth, *Astrobiology*, 8(6), 1127–1137.
- Hofmann, B. A., M. Helfer, L. Diamond, I. M. Villa, R. Frei, and J. Eikenberg (2004), Topography-driven hydrothermal breccia mineralization of Pliocene age at Grimsel Pass, Aar massif, Central Swiss Alps, *Schweiz. Mineral. Petrogr. Mitt.*, 84(3), 271–302.
- Holland, H. D. (2006), The oxygenation of the atmosphere and oceans, *Philos. Trans. R. Soc. London, Ser. B*, 361(1470), 903–915.
- Johnson, J. E., A. Gerpheide, M. P. Lamb, and W. W. Fischer (2014), O₂ constraints from Paleoproterozoic detrital pyrite and uraninite, *Geol. Soc. Am. Bull.*, 126(5–6), 813–830.
- Konhauser, K. O., et al. (2011), Aerobic bacterial pyrite oxidation and acid rock drainage during the Great Oxidation Event, *Nature*, 478(7369), 369–373.
- Kurzweil, F., M. W. Claire, C. Thomazo, M. Peters, M. Hannington, and H. Strauss (2013), Atmospheric sulfur rearrangement 2.7 billion years ago: Evidence for oxygenic photosynthesis, *Earth Planet. Sci. Lett.*, 366(C), 17–26.
- Lalonde, S. V., and K. O. Konhauser (2015), Benthic perspective on Earth's oldest evidence for oxygenic photosynthesis, *Proc. Natl. Acad. Sci., U.S.A.*, 112(4), 995–1000.
- Li, W., A. D. Czaja, M. J. Van Kranendonk, B. L. Beard, E. E. Roden, and C. M. Johnson (2013), An anoxic, Fe(II)-rich, U-poor ocean 3.46 billion years ago, *Geochim. Cosmochim. Acta*, 120(C), 65–79.
- Lüttge, A., R. S. Arvidson, and C. Fischer (2013), A stochastic treatment of crystal dissolution kinetics, *Elements*, 9(3), 183–188.
- Lyons, T. W., C. T. Reinhard, and N. J. Planavsky (2014), The rise of oxygen in Earth's early ocean and atmosphere, *Nature*, 506(7488), 307–315.
- Miller, C. A., B. Peucker-Ehrenbrink, B. D. Walker, and F. Marcantonio (2011), Re-assessing the surface cycling of molybdenum and rhenium, *Geochim. Cosmochim. Acta*, 75, 7146.
- Ohmoto, H., Y. Watanabe, A. C. Lasaga, H. Naraoka, I. Johnson, J. Brainard, and A. Chorney (2014), Oxygen, iron, and sulfur geochemical cycles on early Earth: Paradigms and contradictions, *Geol. Soc. Am. Spec. Pap.*, 504, 55–95.
- Olson, S. L., L. R. Kump, and J. F. Kasting (2013), Quantifying the areal extent and dissolved oxygen concentrations of Archean oxygen oases, *Chem. Geol.*, 362(C), 1–9.
- Pavlov, A. A., and J. F. Kasting (2002), Mass-independent fractionation of sulfur isotopes in Archean sediments: Strong evidence for an anoxic Archean atmosphere, *Astrobiology*, 2(1), 27–41.
- Planavsky, N. J., et al. (2014), Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event, *Nat. Geosci.*, 7(4), 283–286.
- Rasmussen, B., and R. Buick (1999), Redox state of the Archean atmosphere: Evidence from detrital heavy minerals in ca. 3250–2750 Ma sandstones from the Pilbara Craton, Australia, *Geology*, 27(2), 115–118.
- Reinhard, C. T., S. V. Lalonde, and T. W. Lyons (2013), Oxidative sulfide dissolution on the early Earth, *Chem. Geol.*, 362(C), 44–55.
- Ross, S., and A. Sussman (1955), Surface oxidation of molybdenum disulfide, *J. Phys. Chem.*, 59(9), 889–892.
- Rye, R., and H. D. Holland (1998), Paleosols and the evolution of atmospheric oxygen: A critical review, *Am. J. Sci.*, 298(8), 621–672.
- Rye, R., P. H. Kuo, and H. D. Holland (1995), Atmospheric carbon dioxide concentrations before 2.2 billion years ago, *Nature*, 378(6557), 603–605.
- Scott, C., T. W. Lyons, A. Bekker, Y. Shen, S. W. Poulton, X. Chu, and A. D. Anbar (2008), Tracing the stepwise oxygenation of the Proterozoic ocean, *Nature*, 452(7186), 456–459.
- Voegelin, A. R., T. F. Nägler, N. J. Beukes, and J. P. Lacassie (2010), Molybdenum isotopes in late Archean carbonate rocks: Implications for early Earth oxygenation, *Precambrian Res.*, 182(1–2), 70–82.
- Wille, M., J. D. Kramers, T. F. Nägler, N. J. Beukes, S. Schröder, T. Meisel, J. P. Lacassie, and A. R. Voegelin (2007), Evidence for a gradual rise of oxygen between 2.6 and 2.5 Ga from Mo isotopes and Re-PGE signatures in shales, *Geochim. Cosmochim. Acta*, 71, 2417.
- Wille, M., O. Nebel, M. J. Van Kranendonk, R. Schoenberg, I. C. Kleinhanns, and M. J. Ellwood (2013), Mo–Cr isotope evidence for a reducing Archean atmosphere in 3.46–2.76 Ga black shales from the Pilbara, Western Australia, *Chem. Geol.*, 340(C), 68–76.
- Zerkle, A. L., M. W. Claire, S. D. Domagal-Goldman, J. Farquhar, and S. W. Poulton (2012), A bistable organic-rich atmosphere on the Neoproterozoic Earth, *Nat. Geosci.*, 5, 359.
- Zhao, C., J. Chen, X. Long, and J. Guo (2013), Study of H₂O adsorption on sulfides surfaces and thermokinetic analysis, *J. Ind. Eng. Chem.*, 20, 605–609.