

Comment on “The experimental determination of hydromagnesite precipitation rates at 22.5–75°C” by Berninger, U.-N., Jordan, G., Schott, J. and Oelkers, E.H.

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[Received 13 August 2016; Accepted 8 March 2017; Associate Editor: Karen Hudson-Edwards]

ABSTRACT

In this work, we tested the equilibrium constant of hydromagnesite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ at 22.5°C proposed by Berninger *et al.* (2014) against field observations. By field observations we mean that analytical results originate from samples in the natural environment. In our test, we calculated saturation states of hydromagnesite, using the equilibrium constant of hydromagnesite at 22.5°C from Berninger *et al.*, for the carbonate lakes in Qinghai-Xizang Plateau in China and for Salda Lake in Turkey, based on the hydrochemical data from literature. The predictions based on this equilibrium constant indicate that all of these lakes are strongly under-saturated with respect to hydromagnesite. However, hydromagnesite has been shown to form in all of these lakes. Therefore, this equilibrium constant is clearly in direct contradiction with field observations, leading to the conclusion that the equilibrium constant of hydromagnesite of Berninger *et al.* (2014) is not suitable for geochemical modelling.

KEYWORDS: hydromagnesite precipitation, Qinghai-Xizang Plateau, China, Berninger, Salda Lake, Turkey.

Introduction

CORRECT equilibrium constants for hydromagnesite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$, referred to as hydromagnesite (5424) (Xiong and Lord, 2008; Xiong, 2011a), and also called light hydromagnesite to distinguish it from heavy hydromagnesite, dynin-gite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (Botha and Strydom, 2001), are important for the reliable geochemical modelling of many processes. For instance, in the field of nuclear waste management, the assemblage of brucite $[\text{Mg}(\text{OH})_2]$ -hydromagnesite (5424) can be used to buffer the fugacity of $\text{CO}_2(\text{g})$ in geological repositories (Xiong and Lord, 2008) where industrial grade periclase (MgO) or Mg $(\text{OH})_2$ is used as an engineered barrier, such as in the Waste Isolation Pilot Plant in the USA, and in

the Asse repository in Germany. Laboratory measurements should be consistent with field observations. If they are inconsistent with field observations, those laboratory measurements should be considered invalid. To this end, we tested the equilibrium constants of hydromagnesite (5424) suggested by Berninger *et al.* (2014) against field observations to determine if they are consistent with the field observations.

This work focuses on hydromagnesite (5424) which for simplicity, is abbreviated as hydromagnesite.

Berninger *et al.* (2014) published their work on hydromagnesite equilibrium constants and hydromagnesite precipitation kinetics at 22.5°C, 50°C and 75°C. Berninger *et al.* (2014) used the solubility constants of hydromagnesite proposed by their colleagues at Toulouse (see Xiong, 2016, for details) as references to show the correctness of their values. However, those reference values have been demonstrated to be incorrect (Xiong, 2016). If

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<https://doi.org/10.1180/minmag.2017.081.019>

the erroneous reference values are not taken into consideration, the correctness of the equilibrium constants of hydromagnesite suggested by Berninger *et al.* (2014) becomes doubtful.

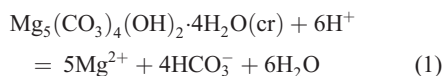
Test of the equilibrium constant of hydromagnesite at 22.5°C

Test objective

Our comment focuses on the equilibrium constant of hydromagnesite at 22.5°C proposed by Berninger *et al.* (2014), as there are well-established field observations at ambient temperatures that can be used as a control. We selected the carbonate lakes in Qinghai-Xizang Plateau in China (Zheng and Liu, 2009) and Salda Lake in Turkey (Suner, 2000; Sezer, 2004) as our primary test objects because hydromagnesite is known to form there and because they have well-established hydrochemical data. Those data are included in Appendix A and Appendix B (deposited with the Principal Editor of *Mineralogical Magazine* and available from http://www.minersoc.org/pages/e_journals/dep_mat_mm.html). Our test hypothesis is that if saturation indices calculated based on the equilibrium constant of hydromagnesite from Berninger *et al.* (2014) show otherwise, their solubility constant should be rejected.

Saturation index calculations

A saturation index is defined as $\log\left(\frac{Q}{K^0}\right)$, where Q is the ion activity product and K^0 is the thermodynamic equilibrium constant for the solid of interest. For hydromagnesite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}(\text{cr})$, K^0 can be expressed as,



$$K_1^0 = \frac{(a_{\text{Mg}^{2+}})^5 \times (a_{\text{HCO}_3^-})^4 (a_{\text{H}_2\text{O}})^6}{(a_{\text{H}^+})^6} \quad (2)$$

In the work of Berninger *et al.* (2014), $\log_{10} K_1^0$ at 22.5°C was evaluated as 33.7. Note that the term for water activity was omitted in the expression for calculation of the equilibrium constant of hydromagnesite in Berninger *et al.* (2014) (equation 2 in Berninger *et al.*, 2014). Saturation indices in our study are calculated by using the computer code *EQ3/6 Version 8.0a* (Wolery *et al.*, 2010; Xiong, 2011a).

Saturation states with respect to hydromagnesite in the Chinese and Turkish lakes

For the first example, we utilized the hydrochemical data for the carbonate lakes in which hydromagnesite forms, in Qinghai-Xizang Plateau in China (Zheng and Liu, 2009), for calculations of saturation states of hydromagnesite in those lakes. We first converted their hydrochemical data on a molar scale into those on a molal scale using the density function in the *Fracture Matrix Transport (FMT)* code (Babb and Novak, 1997; Wang, 1998; Xiong *et al.*, 2010).

Then, we used *EQ3/6 Version 8.0a* (Wolery *et al.*, 2010; Xiong, 2011a) with an updated thermodynamic database, *DATA0.FM2*, using the Pitzer model for activity coefficients (Xiong and Domski, 2016). As illustrated by Fig. 1, the equilibrium constant of hydromagnesite from Berninger *et al.* (2014) predicted incorrectly that all of the carbonate lakes are strongly under-saturated with respect to hydromagnesite, which directly contradicts field observations. These lakes have a wide range of ionic strengths from dilute to $\sim 6 \text{ mol kg}^{-1}$ (Fig. 1). For comparison, we also employed the equilibrium constant of synthetic hydromagnesite from Xiong (2011b) to make parallel predictions. As indicated by Fig. 1, in contrast, the value from Xiong (2011b) correctly predicts that those carbonate lakes are saturated with hydromagnesite, which is strongly supported by the field observations.

For the second example, we utilized hydrochemical data for Salda Lake, Turkey (Sezer, 2004), in which hydromagnesite forms, for calculations of saturation states of hydromagnesite in this lake. We followed the same procedure outlined above to perform the saturation index calculations with respect to hydromagnesite.

Salda Lake is slightly geochemically and thermally stratified (Sezer, 2004). In the sampling performed by Sezer (2004), the temperature at the surface ranged from 28°C to 28.3°C. At the depth of 20 m, the temperature ranged from 25 to 26.2°C. At the depth of 40 m, the temperature ranged from 21 to 22.5°C. At the depth of 60 m, the temperature ranged from 17 to 18.5°C. As shown in Figs 2a–d, according to the equilibrium constant of hydromagnesite from Berninger *et al.* (2014), Salda Lake is strongly under-saturated with respect to hydromagnesite in the waters at all levels of the lake, including the surface water (Fig. 2a), the water at 20 m below the lake surface (Fig. 2b), the water at 40 m below the lake surface (Fig. 2c), and the water

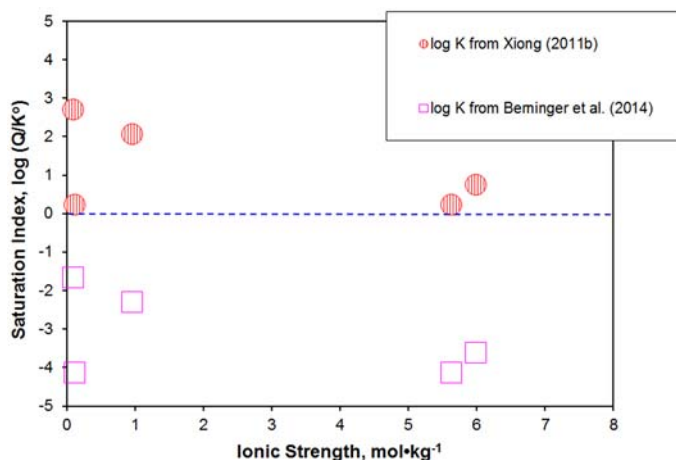


FIG. 1. Saturation indices versus ionic strength of hydromagnesite for the carbonate lakes in Qinghai-Xizang Plateau, China, based on the solubility constants of hydromagnesite, from Xiong (2011b) on synthetic hydromagnesite and Berninger *et al.* (2014). The hydrochemical data are from Zheng and Liu (2009).

at 60 m below the lake surface (Fig. 2d). Notice that the ionic strengths of the waters from the Salda Lake are low. Therefore, in order to show the small variations, the scale of x axis in Figs 2a–d is 10^{-2} mol·kg⁻¹ in ionic strength.

In particular it should be pointed out and emphasized that the starting material, hydromagnesite, for the dissolution experiments in Berninger *et al.* (2014), was from Salda Lake. The strong undersaturation with hydromagnesite in Salda Lake depicted by the equilibrium constant from Berninger *et al.* (2014), as indicated by Figs 2a–d, simply cannot be reconciled with the field observations. Thus, the equilibrium constant of hydromagnesite from the work of Berninger *et al.* (2014), including the dissolution experiments using hydromagnesite from Salda Lake, is in direct conflict with the observation that hydromagnesite forms in Salda Lake.

The predictions based on the equilibrium constant of synthetic hydromagnesite from Xiong (2011b) are also presented for comparison (Figs 2a–d). The predictions using the value from Xiong (2011b) suggest that the surface water and the water at the depth of 20 m below the surface of Salda Lake are slightly oversaturated with respect to hydromagnesite (Figs 2a and b). The water at the depth of 40 m is saturated with hydromagnesite (Fig. 2c), while the water at the depth of 60 m is slightly under-saturated with respect to hydromagnesite. These predictions are consistent with the field observations (Suner, 2000).

It is not certain why the experiments in the work of Berninger *et al.* (2014) gave results inconsistent with field data. One of the most likely causes could be that equilibrium was not attained in their experiments. It is worth noting that the duration of their experiments was short, usually ~5 days. In contrast, the experimental duration in Xiong (2011b) was at least ~700 days.

Summary

In this work, we have demonstrated that the equilibrium constant of hydromagnesite at 22.5°C from Berninger *et al.* (2014) contradicts field observations, leading to the conclusion that their equilibrium constant is incorrect and unsuitable for any reliable geochemical modelling.

The predictions based on the Berninger *et al.* (2014) value suggest that the carbonate lakes in Qinghai-Xizang (Tibet) Plateau in China and Salda Lake in Turkey are strongly under-saturated with respect to hydromagnesite, implying that hydromagnesite should not form in these lakes. These predictions are inconsistent with the field observations, as hydromagnesite forms in these lakes. Of particular concern is that the starting material, hydromagnesite, for their dissolution experiments was from Salda Lake, so their equilibrium constant should reproduce the field observations in the Salda Lake.

We suspect that the equilibrium constants for hydromagnesite from Berninger *et al.* (2014) at 50°C

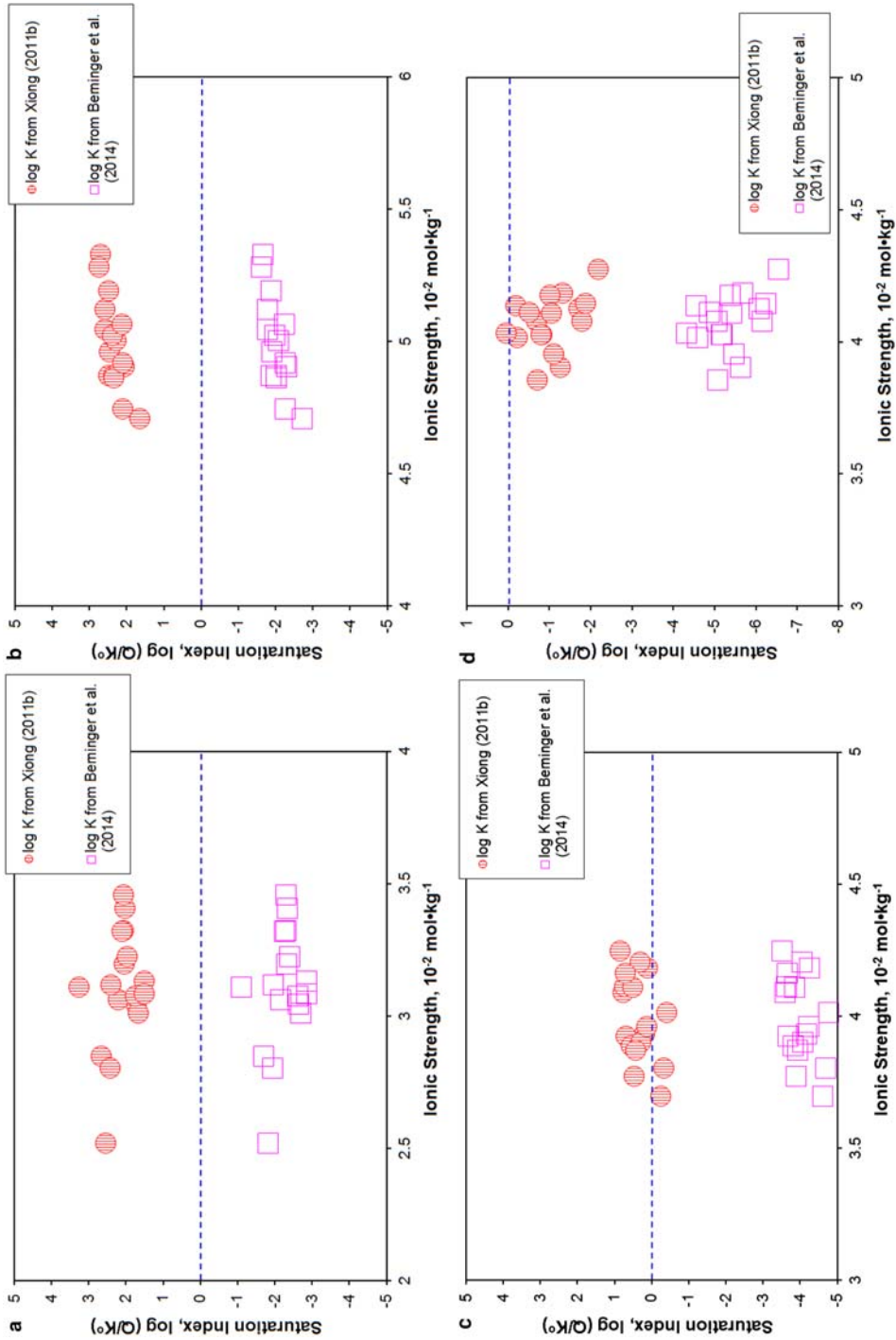


FIG. 2. A plot showing saturation indices of hydromagnesite for the water in Saldia Lake, Turkey, based on the solubility constants of hydromagnesite, from Xiong (2011b) on synthetic hydromagnesite and Beminger *et al.* (2014). (a) Surface water; (b) the water at 20 m below the lake surface; (c) the water at 40 m below the lake surface; (d) the water at 60 m below the lake surface. The hydrochemical data are from Sezer (2004).

and 75°C might also have similar shortcomings. Berninger *et al.* (2014) also utilized the values at these two temperatures proposed by their colleagues at Toulouse as references to show the correctness of their own values. As the values at elevated temperatures proposed by their colleagues at Toulouse have also been questioned (Xiong, 2016), because of their errors in calculating equilibrium constants without consideration of simultaneous equilibrium with brucite, we have similar doubts about the correctness of the equilibrium constants at 50°C and 75°C from Berninger *et al.* (2014). At this time, we refrain from commenting in detail further on their values at 50°C and 75°C.

Acknowledgements

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. This research is funded by WIPP programs administered by the Office of Environmental Management (EM) of the U.S. Department of Energy. SAND2016-7691J. The authors would like to thank Dr. Peter Williams, the journal Principal Editor, for his consideration of this comment. The authors also thank the journal reviewers for their comments, and Dr. Karen Hudson-Edwards, the Associate Editor, for her time.

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