HYDROTHERMAL RARE EARTH ELEMENT (XENOTIME) MINERALIZATION AT MAW ZONE, ATHABASCA BASIN, CANADA, AND ITS RELATIONSHIP TO UNCONFORMITY-RELATED URANIUM DEPOSITS—A REPLY

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Sir: The question raised by Burlinson (2018) about the validity of hydrogen gas (H₂) data as determined by mass spectrometry is not a new one. The same question was raised five years ago by Burlinson (2013) and was rebutted by Hofstra and Landis (2013), who defended the validity of their data and pointed out that Burlinson's perception of the analytical procedure of mass spectrometry and preservation of H₂ in fluid inclusions was incorrect. Although Burlinson (2018) recognized that the low levels of H₂ in our analytical results (Rabiei et al., 2017) have no impact on our mineralization models or conclusions, he insisted that "it is highly misleading to report such H₂ analyses, as H₂ is an instrumental artifact of the mass spectrometer ionizer and not a component of the fluid inclusion volatiles at all" (p. 997). We would like to take this opportunity to further clarify Burlinson's misperception of the issue and make two important points: (1) H₂ is a common component in geologic fluids, and it is normal to detect it in fluid inclusions, and (2) the mass spectrometric analytical procedure that was used in our study (Rabiei et al., 2017) has already taken into account the background H₂ that might be produced in the ionization process, and the data reported are above background and above the blanks.

 H_2 in geologic fluids can be produced by two major processes in geologic environments-i.e., radiolysis of water (dissociation of water molecules by ionizing radiation) and water-rock reaction (e.g., 3FeO (in silicates) + $H_2O = Fe_3O_4$ $(magnetite) + H_2 (aq.))$ —and H₂-rich fluids have been widely documented in hydrothermal vents and seafloor spreading centers as well as saline fracture waters in Precambrian continental crustal rocks (Sherwood Lollar et al., 2014). H₂-rich fluid inclusions, as shown by Raman spectroscopic studies, have been reported for samples from uranium (Dubessy et al., 1988; Richard, 2017) and rare earth element (REE) deposits (Vasyukova et al., 2016) as well as melt inclusions (Li and Chou, 2015). Although it has been well established that H_2 in fluid inclusions in quartz may be lost due to diffusion (Kats et al., 1962; Mavrogenes and Bodnar, 1994), it is also known that the diffusion rate exponentially decreases with decreasing temperature (Kats et al., 1962; Mavrogenes and Bodnar, 1994; Li and Chou, 2015) such that H₂ diffusion in quartz may be insignificant below 200° to 300°C (Morgan et al., 1992, 1993; Hall and Sterner, 1995). Therefore, preservation of H₂ in fluid inclusions in quartz is not a problem in many geologic environments.

Variable amounts of H_2 were detected in fluid inclusions from uranium deposits (Chi et al., 2017; Liang et al., 2017) as well as REE deposits (Vasyukova et al., 2016) using the same mass spectrometric analysis method as in Rabiei et al. (2017). The fact that H_2 was detected by both Raman spectroscopy and mass spectrometry (Vasyukova et al., 2016) clearly indicates that H_2 is present in the fluid inclusions studied and is not an artifact. The low concentrations of H₂ in the fluid inclusions from the Maw zone REE deposit (Rabiei et al., 2017, table 4), which are below the Raman detection limit, are consistent with the low-U nature of the ore fluid and the oxidizing ambient conditions at the site of mineralization. Nevertheless, the trace amounts of H_2 detected by mass spectrometry are not artifacts: the ore fluid represents a reducing fluid derived from the basement as discussed in Rabiei et al. (2017), and trace amounts of H₂ can be readily derived from the basement. In fact, the Maw zone REE deposit is located in a regional-scale alteration corridor, where a number of worldclass uranium deposits occur (Rabiei et al., 2017). The presence of H₂-rich fluids in the basement is recorded by fluid inclusions in metamorphic rocks near the Gryphon U deposit, which is less than 7 km from the Maw zone REE deposit, and by fluid inclusions in drusy quartz associated with the McArthur River uranium deposit, which is about 40 km to the north, both showing a prominent Raman peak at 4,157 to $4,158 \text{ cm}^{-1}$, diagnostic of H₂ (Fig. 1).



Fig. 1. Raman spectra of an H_2 -rich fluid inclusion in a metamorphic rock near the Gryphon uranium deposit (a) and H_2 -rich fluid inclusions in a drusy quartz associated with the McArthur River uranium deposit (b), located about 7 and 40 km away from the Maw zone REE (xenotime) deposit, respectively.

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The experimental procedure of mass spectrometry used in our study (Rabiei et al., 2017) has been explained in detail in Blamey (2012) and Blamey et al. (2015). The correlation between mass 2 and the water at mass 18 has been recognized for a long time, and a correction for this phenomenon has always been applied in all our fluid inclusion gas analyses. We experimented in moving the channel to slightly off peak as well as changing the background position adjacent to mass 2, but this did not negate the need for a correction. Burlinson (2018) does not present mass spectrometry data to support his thesis, and we find it highly irregular that Burlinson's own references lack peer review. Citing his own web pages, not peer-reviewed journal articles, implies that his assertion is an opinion article rather than a robust discussion. Burlinson's criticism of our work further reflects his unfamiliarity with the analytical procedures commonly exercised in mass spectrometry, as already pointed out by Hofstra and Landis (2013).

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