



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

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Sir: In their paper, “Hydrothermal Rare Earth Element (Xenotime) Mineralization at Maw Zone, Athabasca Basin, Canada, and Its Relationship to Unconformity-Related Uranium Deposits,” Rabiei et al. (2017) report the analysis of hydrogen gas within bulk fluid inclusions in quartz samples using mass spectrometry. Although they report only minor levels of H₂ with no impact on their ore formation models or conclusions, 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. Diatomic hydrogen is generated from a side reaction of monatomic H⁺ and H₂O within the ionizer as explained by Burlinson (<http://appliedminex.com/h2>), which renders any H₂ analysis meaningless. This problem has been further discussed by Burlinson (2013).

Mass spectrographic residual gas analyses are routinely done to determine the quality of high-vacuum systems, and these show the presence of H₂, mass 2, although H₂ is not present in air (P. Hofmann, http://philiphofmann.net/ultra-highvacuum/ind_RGA.html). The H₂ peak either is not discussed or is attributed to water (without explanation) by the manufacturers of these instruments. It is clear that the dissociation of water in the ionizer is the source of H₂, mass 2, in these analyses.

The ionization of water molecules by electron impact gives H₂O⁺ due to removal of an electron. This species is unstable and decomposes into either (H⁺ and OH) or (H and OH⁺). The monatomic H⁺ does not interfere with the analysis of diatomic H₂, so it is wrongly assumed that there is no problem in analyzing for H₂ gas in the original fluid. However, there is a side effect that occurs within the ionizer and converts some of the monatomic H⁺ into diatomic H₂, causing severe interference and negating any meaningful attempt to measure the H₂ gas content of the fluid inclusion volatiles.

It is well known that water molecules “adhere” to all the surfaces in the instrument, including the negatively charged focusing and collimation electrodes, even within ultrahigh

vacuum. In fact, it is typically necessary to bake the equipment for hours at 200°C to remove water if a “dry” vacuum is required, but fluid inclusion volatiles introduce copious quantities of water and the system is operating in a “wet” vacuum. The H⁺ ions produced in the ionizer have random velocities and must be collimated to produce the beam of particles for use in the mass separation stage. Mass spectrometer manufacturers estimate that only about 1% to 3% of the H⁺ ions contribute to the beam; the remaining 97% to 99% of the H⁺ ions are attracted to and impact the negatively charged surfaces of the apparatus. However, these surfaces are all coated with a multimolecular layer of water, resulting in high-energy collisions of H⁺ ions with H₂O molecules on the electrode surfaces. These collisions produce H₃O (hydronium), a species common in interstellar space, which is an environment not dissimilar to the mass spectrometer vacuum (http://en.wikipedia.org/wiki/Hydronium#Interstellar_H3O.2B). Hydronium is unstable and decomposes to produce H₂ (mass 2), which is then ionized, causing H₂ analyses that are nothing but spurious analytical interference resulting from the interaction between H⁺ from water ionization and water molecules in the ionizer. The long mean-free path of ions in the vacuum is irrelevant as the interaction occurs at the water-coated, negatively charged electrodes, where interaction between water and H⁺ is certain and frequent.

H₂ analyses of aqueous fluid inclusion volatiles using mass spectrometry are meaningless and misleading. They should not be reported as results, nor should such H₂ results be used to infer or calculate the redox potential of such fluids.

REFERENCES

- Burlinson, K., 2013, Ore genesis constraints on the Idaho cobalt belt from fluid inclusion gas, noble gas isotope, and ion ratio analyses—a discussion: *Economic Geology*, v. 108, p. 1211–1212.
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