DISCUSSION

ORE GENESIS CONSTRAINTS ON THE IDAHO COBALT BELT FROM FLUID INCLUSION GAS, NOBLE GAS ISOTOPE, AND ION RATIO ANALYSES—A DISCUSSION

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Sir: In their paper, "Ore genesis constraints on the Idaho cobalt belt from fluid inclusion gas, noble gas isotope, and ion ratio analyses," Landis and Hofstra (2012) report on the analysis of hydrogen gas within fluid inclusions using mass spectrometry. They indicate surprisingly high hydrogen contents in fluid inclusions (~25,000 ppm) in this and their other, previous work that they reference. But it is highly unlikely that hydrogen is really that common in geofluids and even less likely that it could remain trapped in fluid inclusions for geological time periods because hydrogen diffuses easily through most materials, including quartz. The laser Raman method for analysis of gas contents of fluid inclusions can also measure hydrogen contents, but such analyses never find the presence of hydrogen within inclusions. The only detection of hydrogen in fluid inclusions by laser Raman that I am aware of was by Dubessy et al. (1988) and the hydrogen was present due to radiolytic dissociation of water within inclusions in a uranium deposit.

These contradictions in the measurement of hydrogen in fluid inclusions are most likely a problem within the method of mass spectrometric analysis for hydrogen in aqueous fluids, as occur in fluid inclusions. It is inappropriate to rely solely on this analytical technique to measure hydrogen contents of fluid inclusions as hydrogen is, in fact, a by-product of the ionizer in the mass spectrometer. In the absence of careful corrections for this spurious hydrogen generation, or confirmation by laser Raman analysis, measurements of hydrogen in aqueous fluids using the mass spectrometric method are highly suspect.

Mass spectrometers have become such common "black box" devices in laboratories that no one now thinks about their inner workings. But a critical part of these instruments is the ionizer, which produces positive ions from the neutral analyte molecules. There are many different types of ionizer, but no papers actually bother to mention which ionizer type was used or its operating conditions. Only the U.S. Geological Survey website mentions that the "electron impact" ionizer is used, as it is in fact for all mass spectrometric analyses of fluid inclusion fluids. This ionizer is the molecular equivalent of an atom-smashing cyclotron and blasts 100 eV electrons at molecules, in which typical covalent bond strengths are only 5 eV. The desired ionization of these molecules is accompanied by extreme molecular fragmentation, as is well known among spectroscopists. The problem is that an extremely common by-product fragment is hydrogen, which is formed from every hydrogenous species in the analyte, including the abundant

water. So analyses of aqueous fluids can potentially show extreme hydrogen contents caused not by the presence of hydrogen, but from analytical by-products as a consequence of the ionization process in the mass spectrometer.

Most of the hydrogen by-product from water ionization occurs as uncharged atoms of mass 1. The analyses for hydrogen gas are done on H_2^+ with mass to charge ratio (m/z) of 2. These 2 species are theoretically separate and it is assumed that the by-product H atoms do not contribute to the H_2 response. However, many spectrograms of residual gas (air and moisture) have substantial peaks at m/z = 2 and Figure 1 shows this very prominent peak at m/z = 2 on an empty vacuum chamber with moisture. Surprisingly high H_2^+ results have also been reported in mass spectrometer analyses by D. Gaboury (2011). This sample consisted of crushed grains of Proterozoic quartz and it is highly unlikely that any hydrogen could still be trapped in these fluid inclusions.

These inexplicably high hydrogen analyses only occur when using mass spectrometry. It is probable that conversion of neutral H and H^+ to H_2 and H_2^+ must be occurring in the ionizer and a proposed mechanism for this is explained by Burlinson (2013). Perhaps it is facilitated by the unusually long residence time of the uncharged H atoms in the ionizer as they are not removed by electrode attractions. Nor is the hydrogen removed very well by turbomolecular vacuum pumps as pumping varies exponentially with the square root of the molecular weight. In addition, ionization of water directly produces some H_2^+ component, as documented by King and Price (2008), who tabulated the relative partial ionization cross sections for the ion fragments from water ionization by the electron ionizer at different voltages. Their data
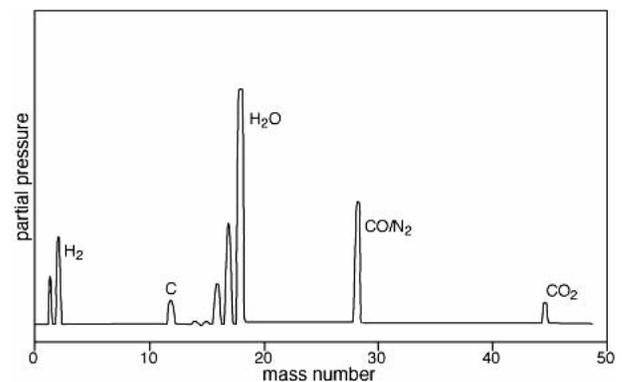

FIG. 1. Mass spectrogram of moisture and residual air in a vacuum chamber. Note the substantial H_2 peak, which is attributed to water in the analyte (from http://philiphofmann.net/ultrahighvacuum/ind_RGA.html).

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show that H_2^+ has a relative cross section of 0.00113, compared with the species H_2O^+ at 100 volts while H^+ has a relative cross section of 0.240.

Although the ionization of water directly produces only a small quantity of H_2^+, significant additional H_2^+ is apparently produced by interactions between the abundant H and H^+ that are only inefficiently removed from the vacuum. It is surely necessary to correct any estimate of H_2 in the analyte for these serious interferences caused by hydrogen by-products during the ionization of water molecules in the mass spectrometer. Other hydrogenous species, including hydrocarbons, will also produce hydrogen fragments in the ionizer and must also be corrected for. But I have seen no attempt by any mass spectrometer operators to do this. In part this is due to a scarcity of information on the relative partial ionization cross sections for H, H^+ and H_2^+ production from all the hydrogenous molecules concerned. But without these critically important corrections we should be extremely sceptical of measurements of hydrogen in fluid inclusion fluids using mass spectrometry and should instead rely on the laser Raman method to analyze for hydrogen.

Additional discussion of the problems of using mass spectrometry to determine the hydrogen content of fluid inclusion fluids is at http://www.appliedminex.com/h2.htm.

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ORE GENESIS CONSTRAINTS ON THE IDAHO COBALT BELT FROM FLUID INCLUSION GAS, NOBLE GAS ISOTOPE, AND ION RATIO ANALYSES—A REPLY

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Sir: Burlinson (2013) questions the veracity of the H_2 concentrations reported for fluid inclusion extracts from minerals in the Idaho cobalt belt (Table 2; Landis and Hofstra, 2012) and suggests that they are an analytical artifact of electron-impact mass spectrometry. He also declares that H_2 should not be present in fluid inclusions because it is invariably lost by diffusion and is never detected in fluid inclusions by laser Raman. We welcome this opportunity to reply and maintain that the reported H_2 contents are accurate. Below we explain why Burlinson's criticisms are invalid.

Burlinson (2013, p. 1211) begins by stating that "… it is highly unlikely that hydrogen is really that common in geofluids…." Although H_2 is a trace component of ordinary geochemical environments, most ore-forming environments are extraordinary. In fact, numerous studies of modern magmatic and hydrothermal systems have shown that H_2 is present in detectable amounts and that it actually participates in a variety of important redox and sulfidation reactions (Einaudi et al., 2003). Consequently, H_2 measurements are used to calculate the redox parameter R_H and the sulfidation state parameter R_S (Giggenbach, 1987) and are employed in the H_2-CH_4-CO_2-H_2S geothermometer (D'Amore and Panichi, 1980).

The redox environment in the Idaho cobalt belt is key to the abundance of H_2 in associated fluids. Several observations indicate the chemical environment in this belt was reduced before, during, and after mineralization. The argillite layers in the host rocks are commonly black due to the presence of graphitized organic carbon. Unlike typical iron oxide copper-gold (IOCG) deposits, the ores generally lack magnetite or hematite. Instead, they contain an abundance of Fe-rich biotite (dark green annite) and tourmaline (black schorl-dravite) with divalent iron. In comparison to magnetite, annite is stable at high f_{H_2} (Fleet, 2003) and its Fe^{2+}/Fe_{Total} ratio is governed by f_{H_2} via the oxybiotite reaction (Fe^{2+} + OH^- $\rightleftharpoons$ Fe^{3+} + O^{2-} + $\frac{1}{2}H_2$; Rancourt et al., 2001). All of the tourmalines analyzed by Trumbull (2011) are Al saturated and, thus, contain predominantly ferrous iron. The red metamorphic garnets analyzed by Eiseman (1988) are almandine ($Fe_3Al_2Si_3O_{12}$) with ferrous iron. Fluid inclusion extracts from ore-related sulfides, quartz, and annite as well as post-ore quartz and metamorphic garnet contain significant CH_4. The calculated H_2-CH_4-CO_2-H_2S temperature for Cretaceous metamorphic garnet is within the range obtained by Eiseman (1988) using the biotite-garnet geothermometer. Such evidence suggests that the Idaho cobalt belt maintained a reducing environment in which H_2 was a stable fluid component.

Burlinson (2013, p. 1211) goes on to state that it is "… even less likely that it [H_2] could remain trapped in fluid inclusions for geological time periods because hydrogen diffuses easily through most materials, including quartz."

Fick's law dictates that the rate of hydrogen diffusion through a host mineral is governed by temperature and the concentration gradient between the fluid inclusion and fluid in adjacent pores. The preservation of H_2 in our samples is consistent with the presence of graphitic carbon and ferrous iron minerals in the Idaho cobalt belt, reducing conditions, small H_2 concentration gradients between fluid inclusions and pore fluids, and low rates of H_2 diffusion. If pore fluids had contained more H_2 than fluid inclusions, then CH_4 concentrations in the inclusions may have increased by the reaction of H_2 with CO_2 to form CH_4 and H_2O. This phenomenon has been documented by Hrsta et al. (2011) in laser Raman studies of fluid inclusions in the Libcice orogenic gold deposit associated with Neoproterozoic black shales in the Bohemian Massif. The detection of H_2 vapor (up to 6 mole %) in multi-solid inclusions at this locality indicates that, under reducing conditions, H_2 can be preserved in quartz for extended periods of time (e.g. since Carboniferous metamorphism). We imagine that mass spectrometric analysis of fluid inclusion extracts from this deposit would yield data similar to ours. If pore fluids in the Idaho cobalt belt had been oxidized and H_2 continually lost from fluid inclusions by diffusion, then the CH_4 and H_2S in fluid inclusions should have been consumed by reaction with H_2O to form CO_2 and SO_2 (CH_4 + $2H_2O$ $\Rightarrow$ CO_2 + $4H_2 \Uparrow$; H_2S + $2H_2O$ $\Rightarrow$ SO_2 + $3H_2 \Uparrow$). The presence of significant CH_4 and H_2S in fluid inclusion extracts suggests that H_2 was retained.

Burlinson (2013, p. 1211) seems to think that H_2 can only be detected reliably by laser Raman and goes on to say that "…laser Raman…analyses never find the presence of hydrogen within inclusions." Hydrogen may rarely be detected in single inclusions by laser Raman because the detection limit is higher than that in fluid inclusion extracts by mass spectrometry. In addition, the spectral region where H_2 is expected to appear, out beyond water at 4156 cm^{-1}, is rarely scanned because H_2 is generally presumed to be absent or undetectable.

Burlinson's (2013, p. 1211) chief criticism is that "in the absence of careful corrections … measurements of hydrogen in aqueous fluids using the mass spectrometric method are highly suspect." He goes on to discuss the importance of taking into account the fragmentation of water and other hydrogen-bearing compounds in the source of the mass spectrometer as well as the background abundance of H_2 in the enclosing vacuum system (7 paragraphs, 1 figure, 1 reference, 1 viewpoint on his company website). This is fundamental mass spectrometry. It is clear that Burlinson didn't read our paper very carefully, nor did he read the references that we cited (Landis and Hofstra, 1991; Landis and Rye, 2005), or he would know that we have always accounted for the fragmentation of each gas species, including water and other gases with fragments at m/z 1 and 2. Though some analysts rely on published tables (e.g., NIST) for gas specific fragmentation and sensitivity data, we analyze mixtures of individual gas

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species with N_2 or Ar to document their relative ionization efficiencies and fragmentation in the source of our quadrupole mass spectrometer. Such calibrations are conducted for each and every filament (e.g., thoriated iridium, tungsten, rhenium). The calibration data are incorporated into the data reduction algorithm, which is comprised of least square residual computations utilizing all mass intensities. The procedure includes background subtraction for both standards and samples, which are measured at comparable pressures (ca. 1×10^{-8} torr). Thus, the background abundance of H_2 in our mass spectrometer is accounted for.

Some may speculate that the H_2 detected is derived from the breakdown of H_2O or CH_4 in our heating vessel during gas extraction at 300°C (sulfides) or 500°C (quartz). We know from numerous experiments and experience running samples from various reduced to oxidized environments that the magnitude of H_2 produced by the breakdown of H_2O and CH_4 at these extraction conditions is very small in comparison to the amount of H_2 obtained. Inspection of our Table 2 (Landis and Hofstra, 2012, p. 1193) shows that some sulfide (sample 2478) and quartz (sample 2498) samples with high concentrations of H_2O and CH_4 have relatively low H_2 abundances (0.1 and 0.6 mole %, respectively). Thus, it is not logical to attribute the high concentrations of H_2 in the other samples to breakdown of H_2O and CH_4. Crushing at ambient temperature doesn't eliminate H_2, as evidenced by recent results from a PGE-bearing quartz vein that, upon crushing, released substantial H_2.

We considered whether the high H_2 concentrations in our samples could have resulted from OH^- mediated thermal oxidation of iron in biotite, as described by Rancourt et al. (2001). However, the amount of H_2 released from a biotite separate (1.1 mole %) is less than that obtained from several samples of quartz as well as tourmaline, sulfide, and garnet (Table 2; Landis and Hofstra, 2012). Thus, even if minute inclusions of biotite were present in these minerals, they cannot account for the amount of H_2 obtained. Although thermal oxidation of Fe in tourmaline also produces H_2, experiments show this reaction begins at temperatures greater than 500°C (Bačík et al., 2011). So, it cannot account for the amount of H_2 (3.4 mole %) released from the tourmaline separate.

We conclude that, with the exception of biotite, our reported H_2 concentrations are representative of the amount present in gas released overwhelmingly from fluid inclusions in each mineral separate analyzed. The results are consistent with other information and support our conclusion that the Idaho cobalt belt is a reduced analog of IOCG systems.

Although bulk methods of fluid inclusion analysis have many limitations, much can be learned from the chemical and isotopic composition of the extracts. We agree that superior interpretations will result from the combination of single and bulk inclusion analyses. This is the direction of current research in the Denver Inclusion Analysis Laboratory (http://minerals.cr.usgs.gov/dial/).

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