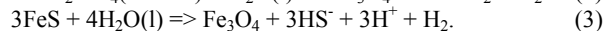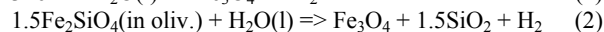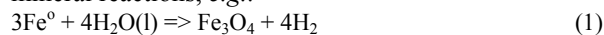**AQUEOUS OXIDATION OF PARENT BODIES OF CARBONACEOUS CHONDRITES AND GALILEAN SATELLITES DRIVEN BY HYDROGEN ESCAPE.**

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Introduction: Chemistry and mineralogy of carbonaceous chondrites and remote sensing data on the Galilean satellites indicate a trend in oxidation of the original material formed in the solar nebula and in the Jovian subnebula. In particular, the presence of sulfates in CM and CI carbonaceous chondrites and on the surfaces of Europa [1] and Ganymede [2], as well as SO_2-rich volcanism on Io indicate profound oxidation of corresponding parent bodies and satellites. Here we propose that oxidation that led to the formation of sulfates in parent bodies of carbonaceous chondrites and Galilean satellites was driven by hydrothermal alteration followed by H_2 escape into space.

Oxidative aqueous processes in asteroids: Chemical and mineralogical signatures in chondrites indicate that they formed under a wide range of redox conditions previously attributed to disparities of the C/O and/or H_2/H_2O ratios in the solar nebula, as well as aqueous processes in parent bodies [3]. The high nominal H_2/H_2O mole ratio ($\sim 2 \times 10^3$) in the solar nebula implies that oxidation mostly occurred inside parent bodies, were melting of accreted water ice created H_2O-rich and H_2-depleted conditions. Indeed, many chemical, mineralogical, and isotopic data, as well as results of age dating, are consistent with aqueous alteration and oxidation on parent bodies [e.g., 3-5]. Correlation of the degree of oxidation observed in carbonaceous chondrites with the extent of aqueous alteration suggests that oxidation was driven by water-mineral reactions, *e.g.:*

$$3Fe^o + 4H_2O(l) \Rightarrow Fe_3O_4 + 4H_2 \qquad (1)$$
$$1.5Fe_2SiO_4(\text{in oliv.}) + H_2O(l) \Rightarrow Fe_3O_4 + 1.5SiO_2 + H_2 \qquad (2)$$
$$3FeS + 4H_2O(l) \Rightarrow Fe_3O_4 + 3HS^- + 3H^+ + H_2. \qquad (3)$$

Hydrogen produced in oxidative reactions like (1)-(3) dissolves into solution, and at some *T-P* conditions can separate into the gas phase. Interaction of Fe metal with H_2O (eq. 1) would lead to H_2 pressures as high as a few kbars and separation of H_2-rich gas is a likely result of that interaction. However at low-pressure conditions in asteroids, reaction (1) cannot rich equilibrium and proceeds until mechanical failure through H_2 overpressuring from inside at pressures < $\sim 10^2$ bar [6] or until consumption of either Fe^o or H_2O is complete. A deficiency of H_2O could account for limited oxidation in parent bodies of ordinary chondrites and CV3 carbonaceous chondrites. If the amount of H_2O was sufficient for total consumption of Fe metal, ferrous silicates and troilite could experience further oxidation. However that oxidation could also be incomplete if H_2O was completely consumed via oxidation
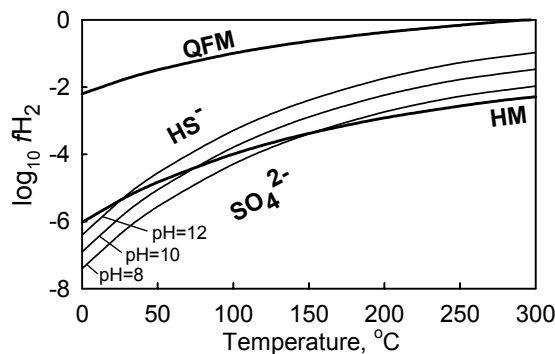

Figure 1. Stability fields of sulfate and bisulfide at a total pressure of 100 bar. The thin solid curves represent equal activities of SO_4^{2-} and HS^- at various pH. The QFM curve represents equilibrium (2) and HM stands for hematite-magnetite buffer. Sulfate is stable at higher temperature and lower fH_2. Low-temperature formation of sulfate in asteroidal environments requires complete oxidation of magnetite and is unlikely (see also [10]).

and serpentinization or if the amount of $H_2(aq)$ reaches equilibrium levels. In a closed system, further oxidation would be prohibited. Although equilibrium models for aqueous alteration on parent bodies of carbonaceous chondrites reveal some oxidation trends [*e.g.,* 7-9], formation of sulfate-rich fluids was not observed. In fact, oxidation of minerals and solutes leading to sulfate formation on parent bodies has not be explained in the framework of closed-system modeling.

Conditions for sulfate formation: Although both alkaline and hydrothermal conditions favor stability of SO_4^{2-} at relatively high fH_2, formation of SO_4^{2-}-rich fluids requires oxidation of solutions beyond conditions at which the fayalite-magnetite association is stable (see Fig. 1). It follows that high concentrations of $H_2(aq)$ produced during early stages of aqueous alteration through reactions (1)-(3) must have greatly decreased by the time of sulfate formation. We propose that the decrease in $H_2(aq)$ content in aqueous solutions, which is required to account for formation of highly oxidized minerals in CM and CI carbonaceous chondrites, was driven by escape of H_2 gas from parent asteroids.

Why and how does H_2 escape? Both thermodynamic and kinetic arguments indicate that hot central zones of a water-bearing asteroid were primarily responsible for H_2 production by reactions like (1)-(3) and separation of H_2 into the gas phase at early stages of alteration. Driven by pore closure through serpentinization, $H_2(g)$ gas migrated into more permeable pe-

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ripheral zones where it would have escaped into space through fissures caused either by collisions with other bodies or by overpressure overcoming the asteroid's internal strength. In addition to escape through fissures, H_2 in the outermost porous zones of asteroids may have diffused into space. In fact, H_2 diffuses and escapes easily, as demonstrated in hydrothermal experiments [11] investigations of fluid inclusions in terrestrial rocks [*e.g.,* 12], and detection of H_2 seepage above altered peridotites [13]. Decompression caused by H_2 escape from an asteroid would trigger further separation of H_2 into a gas phase, and lead to lower concentrations of dissolved H_2, which would, in turn, increase the oxidation potential of asteroidal fluids. Permeability of outer asteroidal zones favors profound oxidation and *vice versa*.

The effect of H_2 escape on the speciation and oxidation state of hydrothermal solutions: To test this idea, hydrothermal alteration calculations were conducted for the Ca-Mg-Fe-Na-K-Si-Al-C-S-Cl-H_2O system (150°C, 1375 bar, water/rock mass ratio of 0.77) in which H_2 loss was modeled by lowering fH_2. The pressure represents conditions at the oceanic floor on Europa, and the water/rock ratio represents interaction of a 100 km thick ocean with 10% of the mass of Europa's mantle. An average CV type carbonaceous chondrite [14] supplied the elemental composition of mantle rocks. The equilibrium speciation was calculated with the EQCHEM code provided by Mikhail Mironenko (Vernadsky Institute, Moscow). Data for minerals are the same as in the SUPCRT92 code [15] and data for aqueous species are from [16,17].

The decrease in fH_2 results in decreases of the concentrations of HS- and $H_2S(aq)$ and an increase in SO_4^{2-} abundance, as shown in Fig. 2a. Until log fH_2 drops to about -1.0, a gas phase exists in equilibrium with the minerals and aqueous solution and is rich in CH_4, H_2, and H_2O (Fig. 2c). In reality, formation of CH_4 could be inhibited, and the fraction of H_2 in the gas phase would be higher than calculated here. If CH_4 was formed (in part as a result of hydrogenation of meteoritic organic compounds), its escape should contribute to oxidation. Formation of the magnetite-serpentine association and the appearance of carbonates and sulfates mark advanced stages of oxidative aqueous alteration (Fig. 2d). The whole mineral assemblage, which in our example models hydrothermal systems on Europa, roughly resembles products of aqueous alteration observed in CM and CI carbonaceous chondrites. Note that at lower pressures in asteroids, $H_2(g)$ would separate at lower fH_2 values than on Europa.

Conclusion: Formation of oxidized sulfate-bearing fluids on parent bodies of carbonaceous chondrites and Galilean satellites required a large decrease in the con-

centration of dissolved H_2 and must have required H_2 loss into space. Rock's alteration followed by H_2 escape seems to be a universal process responsible for oxidation of parent bodies of ordinary and carbonaceous chondrites, all four Galilean satellites, Venus [18] and Mars [19], as well as Earth's ophiolites.

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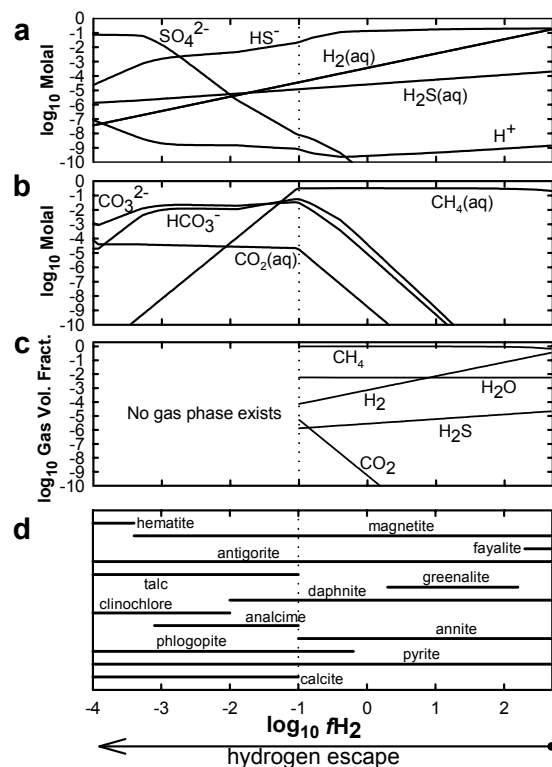

Figure 2. Changes of equilibrium speciation caused by removal of H_2 (see text for details).