

LETTER

Discovery of the first natural hydride

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ABSTRACT

Although hydrogen is the most abundant element in the solar system, the mechanisms of exchange of this element between the deep interior and surface of Earth are still uncertain. Hydrogen has profound effects on properties and processes on microscopic-to-global scales. Here we report the discovery of the first hydride (VH<sub>2</sub>) ever reported in nature. This phase has been found in the ejecta of Cretaceous pyroclastic volcanoes on Mt Carmel, N. Israel, which include abundant xenoliths containing highly reduced mineral assemblages. These xenoliths were sampled by their host magmas at different stages of their evolution but are not genetically related to them. The xenoliths are interpreted as the products of extended interaction between originally mafic magmas and CH<sub>4</sub>+H<sub>2</sub> fluids, derived from a deeper, metal-saturated mantle. The last stages of melt evolution are recorded by coarse-grained aggregates of hibonite (CaAl<sub>12</sub>O<sub>19</sub>) + grossite (CaAl<sub>4</sub>O<sub>7</sub>) + V-rich spinels ± spheroidal to dendritic inclusions of metallic vanadium (V<sup>0</sup>), apparently trapped as immiscible metallic melts. The presence of V<sup>0</sup> implies low oxygen fugacities and suggests crystallization of the aggregates in a hydrogen-rich atmosphere. The presence of such reducing conditions in the upper mantle has major implications for the transport of carbon, hydrogen and other volatile species from the deep mantle to the surface.

**Keywords:** Mantle, hydride, H fluids, crystal structure

INTRODUCTION

Evidence is rapidly accumulating for the widespread presence of highly reduced [low oxygen fugacity ( $f_{O_2}$ )] volumes within the lithospheric mantle, both beneath cratons and in off-craton areas with much thinner lithosphere (Griffin et al. 2018, 2019a). A key indicator of such low  $f_{O_2}$  is moissanite (SiC), which becomes stable at  $f_{O_2}$  ca. 6 log units below that of the iron-wüstite buffer reaction ( $\Delta IW-6$ ). The IW buffer is generally thought to define the minimum  $f_{O_2}$  of both the lithospheric mantle and the deeper mantle (Frost and McCammon 2008). However, SiC with high-temperature metallic inclusions is a relatively common trace phase in heavy-mineral concentrates from kimberlites, lamproites, and similar deep-seated volcanic rocks, and it occurs as an inclusion in diamonds (Shiryaev et al. 2011; Griffin et al. 2018, 2019a). It has also been found in the peridotites and chromitites of many ophiolitic complexes, particularly in the Tethyan belt across Tibet into Turkey, and in the Polar Urals. In these complexes, SiC is usually associated with a suite of other super-reduced (SuR) phases including carbides, silicides, and native metals (Fe, Cr, Ni) and, in some cases, microdiamonds with unusual morphology and isotopic characteristics (Xiong et al. 2017).

At least two off-craton occurrences, at Mt Carmel in northern Israel (Griffin et al. 2016, 2018; Xiong et al. 2017) and Sierra de Comechingones, Argentina (Cámara et al. 2019), now provide

evidence for even lower  $f_{O_2}$ , in the form of V<sup>2+</sup>-bearing oxides, V-Al alloys, and native vanadium in hibonite-grossite-spinel assemblages found as xenolithic fragments in tuffs produced by explosive eruptions. The native metal requires  $f_{O_2}$  of ca.  $\Delta IW-9$ , which suggests the presence of hydrogen-dominated fluids. Here we confirm this suggestion by reporting the discovery of the first natural metal hydride, VH<sub>2</sub>, from the Mt Carmel locality, and discuss the implications for mantle  $f_{O_2}$  and the transfer of fluids in the mantle.

SAMPLES

The xenoliths in which the natural hydride was found occur in the pyroclastic ejecta of small Cretaceous basaltic volcanoes exposed on Mt Carmel and have been sampled from placer gemstone deposits in the Kishon river, which drains Mt Carmel and enters the sea near Haifa in northern Israel (Griffin et al. 2018). They are part of a xenolith assemblage that includes aggregates of skeletal corundum crystals with melt pockets containing reduced mineral assemblages [SiC (moissanite), Fe-Ti-Zr silicides/phosphides, Ti-nitrides, and borides] that require high  $T$  and very low  $f_{O_2}$  (down to  $\leq \Delta IW-7$ ). The xenoliths studied here comprise coarse-grained aggregates of hibonite+grossite+spinel assemblages that carry inclusions of V<sup>0</sup> and V-Al alloys, indicating  $f_{O_2}$  down to  $\leq \Delta IW-9$ . Descriptions of these rocks (Griffin et al. 2016, 2018, 2019a, 2019b; Xiong et al. 2017) have noted the abundance of amorphous carbon in brecciated aggregates, and SiC and TiC in the xenoliths, and suggested that the crystallization of skeletal corundum and

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the unusually low  $f_{O_2}$  reflect the interaction of deep-seated basaltic magmas with mantle-derived  $CH_4+H_2$  at high fluid/melt ratios. This interaction led to the progressive reduction, the desilication of the magma through the immiscible separation of carbon-rich Fe-Ti-silicide melts (abundant in the corundum aggregates), and ultimately to the  $Al_2O_3$ -supersaturation and the rapid growth of skeletal/hopper corundum crystals, which have trapped samples of their parental melts.

The coarse (centimeter-sized crystals) V-bearing hibonite + grossite + spinel aggregates discussed here appear to represent a late, pegmatitic stage of this evolution (Griffin et al. 2019b). The grain sizes, magmatic microstructures, and evidence for an extended sequence of magmatic crystallization (Xiong et al. 2017; Griffin et al. 2018) clearly rule out more speculative origins such as lightning strikes (Ballhaus et al. 2017), meteorite impact, or shallow hydrothermal circulation. Petrographic evidence for the reaction liquid + corundum  $\rightarrow$  anorthite, and the stability of grossite, suggest that this process operated at or near to the base of the crust (25–30 km depth; Griffin et al. 2018), and at temperatures ranging from 1450–1500 °C to a minimum of >1150 °C (see below).

## RESULTS AND DISCUSSION

### Occurrence of vanadium hydride (VH<sub>2</sub>)

The new vanadium hydride was found as one subhedral crystal, about 20  $\mu$ m in size, coexisting with V<sup>0</sup> and (V-Al)-alloys enclosed in hibonite (Fig. 1). Microprobe analysis of this grain (carried out using a CAMECA 100X electron microprobe at 15 kV, 10 nA, 1  $\mu$ m beam size, counting times 20 s for peak and 10 s for background) showed only V, with minor Al (~5 atom%).

To get information on the crystal structure, the small VH<sub>2</sub> fragment was handpicked from the polished section under a reflected light microscope and mounted on a 5  $\mu$ m diameter carbon fiber, which was, in turn, attached to a glass rod. Then the fragment was tested by single-crystal X-ray diffraction. Single-crystal X-ray studies were carried out using a Bruker D8 Venture diffractometer equipped with a Photon III CCD detector, with graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å), and with 100 s exposure time per frame; the detector-to-sample distance was 7 cm.

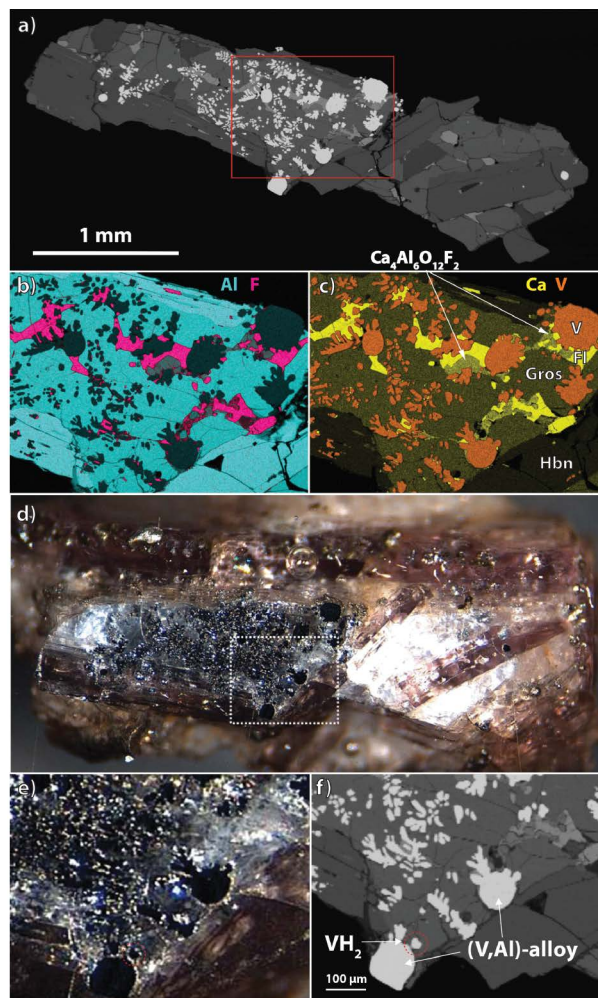
Since we have only one grain, we have avoided destructive analysis to quantify the hydrogen content. The structural data (see below) represent a strong and solid proof in support of the VH<sub>2</sub> stoichiometry.

### Crystal structure of VH<sub>2</sub>

The structure was solved by direct methods and then refined using the program Shelxl-97 (Sheldrick 2008). The site occupation factor (s.o.f.) at the V site was allowed to vary (V vs. Al) using scattering curves for neutral atoms taken from the *International Tables for Crystallography* (Wilson 1992). At the last refinement stage, with anisotropic atomic displacement parameters for V and no constraints, the residual value settled at  $R_1(F) = 0.0134$  for 25 unique reflections and 4 parameters.

Crystallographic data (CCDC 1870868) can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) and are available as supplementary material<sup>1</sup>.

The crystal structure of VH<sub>2</sub> is shown in Figure 2. It shows a



**FIGURE 1.** Images of the rock fragment from Mt Carmel. (a) Backscattered electron image of the hibonite-grossite-spinel aggregate studied. The red box indicates the region enlarged in b and c, which represent X-ray compositional maps. (d) Transmitted-light photo (plane polars) of the rock sample studied, showing inclusions of metallic vanadium in platy hibonite crystals. The white dashed box indicates the region enlarged in e, which is also shown as backscattered electron image (f). Arrows mark the (V,Al)-alloys and the VH<sub>2</sub> fragment that was sampled. (Color online.)

cubic unit cell [ $a = 4.268(1)$  Å;  $Z = 4$ ] and space group  $Fm\bar{3}m$ , with the CaF<sub>2</sub> structure type. The solution of the crystal structure gave the VH<sub>2</sub> stoichiometry, with minor Al substituting for V (i.e., V<sub>0.96</sub>Al<sub>0.04</sub>), in good agreement with the electron microprobe data. The results obtained are in excellent agreement with what has been reported for synthetic VH<sub>2</sub> (Müller and Weymann 1986).

### Thermodynamics of vanadium hydrides

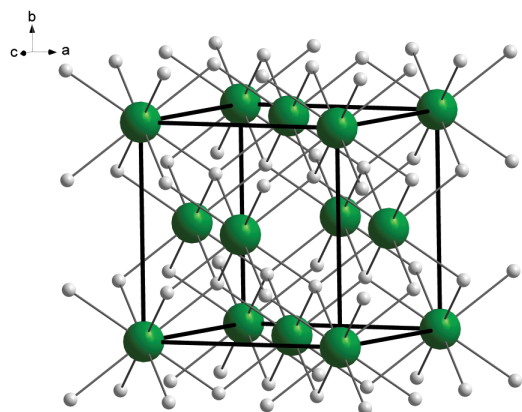
According to Yukawa et al. (2002), vanadium metal absorbs hydrogen and forms first the  $\beta_1$  phase (V<sub>2</sub>H low-temperature phase). Then, as the hydrogenation proceeds, the first-order phase transition from the  $\beta_1$  phase to the  $\beta_2$  phase (V<sub>2</sub>H high-temperature phase) or  $\gamma'$  (VH) takes place. Finally, the  $\gamma$  phase (VH<sub>2</sub>) is formed when it is fully hydrogenated. As a result, there exist two plateaus

in the PCT (pressure-composition-temperature) curve of the V-H system. The first plateau corresponds to the coexistence of the  $\alpha$  phase (hydrogen solid solution phase) and the  $\beta_1$  phase. However, the  $\beta_1$  phase is so stable that the first plateau pressure for this hydride formation is as low as 0.1 Pa at moderate temperatures. Therefore, the hydrogen desorption reaction from the  $\beta_1$  phase never occurs under moderate conditions, for example, at room temperature. On the other hand, the second plateau marks to the coexistence of the  $\beta_2$  phase (VH) and the  $\gamma$  phase,  $\text{VH}_2$ , which corresponds to the natural compound we have identified. As the  $\gamma$  phase is not so stable, its hydrogen absorption and desorption reactions can take place at moderate temperatures and pressures. For this reason, only about half of the hydrogen dissolved in vanadium metal can be used in the subsequent hydrogen absorption and desorption processes.

### Vanadium hydrides at high pressure and temperature

Vanadium hydrides are usually prepared electrolytically by heating vanadium metal with hydrogen (Müller and Weymann 1986). Therefore, the observed abundance of  $\text{V}^0$  and V-Al alloys in our samples may suggest that  $\text{VH}_2$  formed by a localized reaction in the presence of free hydrogen. Suzuki et al. (1989) studied the system (transition metal)-silicate-water at pressures of around 5 GPa and at temperatures ranging from 1000 to 1300 °C using a tetrahedral-anvil high-pressure apparatus and quenching the products isobarically. In their study of the system V-silicate-water, they observed the formation of V-oxide dendrites enclosed in vanadium dihydride,  $\text{VH}_2$ . The petrographic relationships between the two phases clearly showed that hydrogen and oxygen coexisted, dissolved in liquid vanadium, at high pressure and temperature. Such a scenario might be applicable to what is observed in the Mt Carmel samples but with some differences. We found metallic vanadium and (V-Al)-alloys instead of V-oxides, indicating an almost anoxic environment. However, some of the metal inclusions show typical “dense branching structures” (dendrites) (Müller and Weymann 1986; Griffin et al. 2019a) and are associated with sporadic  $\text{VH}_2$ . This represents striking evidence that free hydrogen was present and that it was able to form some  $\text{VH}_2$  from  $\text{V}^0$ .

Experimental data on the V-H system at magmatic temperatures are extremely sparse, but Fukai (2005) has published a phase dia-



**FIGURE 2.** The crystal structure of  $\text{VH}_2$ . Dark green and light gray spheres correspond to V and H atoms, respectively. The unit cell and the orientation of the structure are outlined. (Color online.)

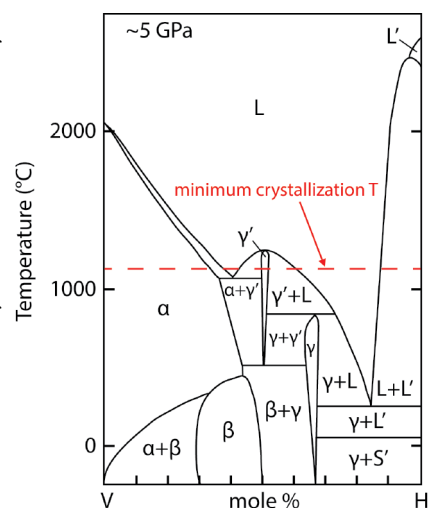
gram for 5 GPa. The melting point of pure vanadium is  $>1900$  °C at 1 atm, rising to ca. 2100 °C at 5 GPa (Fig. 3). However, H is highly soluble in vanadium melts, and lowers the melting point dramatically; the  $\alpha$  phase coexisting with the  $\gamma'$  phase (VH) at the eutectic at ca. 1050 °C has the composition  $\text{V}_{0.7}\text{H}_{0.3}$ . In more H-rich compositions VH is on the liquidus down to a peritectic at ca. 775 °C, where it reacts with the melt to form the  $\gamma$  phase  $\text{VH}_2$ ; this remains the liquidus phase down to ca. 250 °C, and is stable as a solid phase to very low  $T$ . At 1 GPa (the approximate pressure of the Mt Carmel magmatic system; Griffin et al. 2018) these would represent maximum temperatures, assuming that the general pattern of phase relationships shown in Figure 3 remains the same.

The minimum temperature of the Mt Carmel hibonite-grossite-spinel-vanadium assemblages before entrainment and eruption in the host basaltic magmas is constrained by the coexistence of hibonite+grossite + fluorite of the phase  $\text{Ca}_2\text{Al}_3\text{O}_6\text{F}_2$ , which is not stable below 1150 °C at 1 atm (Kim 2011). It is, therefore, unlikely that the  $\text{VH}_2$  sampled here was a liquidus phase. However, as the higher- $T$  vanadium melts cool and crystallize following eruption, they will lose their dissolved  $\text{H}_2$  (Fukai 2005); no H has been observed in three large V balls analyzed by single-crystal X-ray diffraction (Griffin et al. 2019b). We suggest that some of this expelled  $\text{H}_2$  may have been trapped in the outer portions of the melt inclusions, and especially in the sort of smaller protuberances seen in Figure 1. With increasing H/V ratios, this would lead to the subsolidus formation first of VH, then of  $\text{VH}_2$ , and eventually to the remelting and redistribution of  $\text{VH}_2$ , as suggested by the apparent intrusion of “vanadium” melt into the surrounding grossite and fluorite (Fig. 1c).

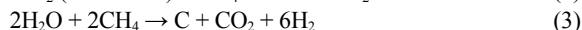
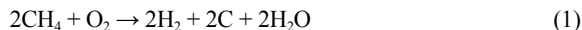
### Generation of free hydrogen in the mantle

The fluids involved in the generation of the ultra-reduced assemblages described here presumably are derived from greater depths and transported upward in association with mantle-derived magmas. The magmas that carried Mt Carmel samples to the surface have been ascribed to “hot-spot” volcanism and carry OIB trace-element and isotopic signatures (Stein and Hofmann 1992). If the sub-lithospheric mantle source of such magmas is metal-saturated (e.g.,  $\Delta\text{IW} = 0$ ), then any C-O-H fluid will be dominated by  $\text{CH}_4$ , with significant contents of  $\text{H}_2$  and lesser amounts of  $\text{H}_2\text{O}$

**FIGURE 3.** Phase diagram of the V-H system at ca. 5 GPa. Diagram redrawn after Fukai (2005). The minimum crystallization temperature (red dashed line) of the oxide-fluoride phases of the matrix is constrained by the presence of  $\text{Ca}_2\text{Al}_3\text{O}_6\text{F}_2$ . (Color online.)



(Frost and McCammon 2008; Matveev et al. 1997). If such fluids are removed to shallower levels, they will either be oxidized by the surrounding FeO-bearing mantle or will impose a low  $f_{O_2}$  on their wall rocks, depending on the local fluid/rock ratio. The oxidation of CH<sub>4</sub> to produce “syngas” is a well-understood industrial process; at pressures >3 kb, where the generation of CO is suppressed, it can proceed by reactions such as:



These reactions are consistent with the abundance of SiC and amorphous carbon in the Mt Carmel assemblages (Griffin et al. 2018). At mantle depths, H<sub>2</sub> and H<sub>2</sub>O are immiscible (Bali et al. 2014); the liberated H<sub>2</sub> would be available to drive further reduction of the local environment to at least  $\Delta\text{IW-9}$ , and to have a major impact on phase relations in coexisting melts and solids.

An alternative mechanism for generating CH<sub>4</sub>-rich fluids (Golubkova et al. 2016) is based on the extraction of oxygen from graphite-saturated COH fluids by oxidation of Fe<sup>2+</sup>, or by removal of carbonate or hydrous phases. Significantly, neither the Mt Carmel nor the Argentinian V-bearing assemblages contain any hydrous phases or carbonates, and none of the oxide or silicate phases in the Mt Carmel corundum xenoliths contain Fe, as all Fe is sequestered in immiscible Fe-Ti-Si-C melts (Griffin et al. 2018). However, mechanisms like that proposed by Golubkova et al. (2016) may have been operative in the early stages of the evolution of the fluid-melt system, and this needs further investigation.

### IMPLICATIONS

The evidence for the presence of CH<sub>4</sub>+H<sub>2</sub>-dominated fluids at Mt Carmel (and elsewhere; Griffin et al. 2018) is a strong argument for the presence of a free metal phase in the sub-lithospheric mantle, buffering  $f_{O_2}$  near IW. This is consistent with other lines of evidence, both theoretical (Rohrbach et al. 2007; Frost and McCammon 2008; Stagno et al. 2013) and physical, in the form of metallic inclusions (accompanied by CH<sub>4</sub>+H<sub>2</sub>) in sub-lithospheric Type II diamonds (Smith et al. 2016, 2018). The movement of such fluids to shallower depths, perhaps through deep-seated volcanism, would allow them to interact with the subcontinental lithosphere, and play an important role in the deposition of carbon as amorphous carbon, graphite or diamonds, depending on the depth of oxidation. The oxidation products of these reactions (CO<sub>2</sub> and H<sub>2</sub>O) may ultimately play an important role in mantle metasomatism (Griffin et al. 2018, 2019a). The presence and movements of such reducing fluids in the upper mantle have major implications for the transport of carbon, hydrogen, and other volatile species from the deep mantle to the surface.

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### Endnote:

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