White Dwarfs as Probes of Fundamental Physics: Tracers of Planetary, Stellar and Galactic Evolution
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Exoplanetary oxygen fugacities from polluted white dwarf stars

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Abstract. The intrinsic oxygen fugacity of a planet profoundly influences a variety of its geochemical and geophysical aspects. Most rocky bodies in our solar system formed with oxygen fugacities approximately five orders of magnitude higher than that corresponding to a hydrogen-rich gas of solar composition. Here we derive oxygen fugacities of extrasolar rocky bodies from the elemental abundances in 15 white dwarf (WD) stars polluted by accretion of rocks. We find that the intrinsic oxygen fugacities of rocks accreted by the WDs are similar to those of terrestrial planets and asteroids in our solar system. This result suggests that at least some rocky exoplanets are geophysically and geochemically similar to Earth.

Keywords. white dwarfs, planetary systems

1. Introduction

White dwarf stars are the last observable stage of stellar evolution for stars less than 8–10 solar masses. WDs are approximately $0.6M_{\odot}$ and $\sim 1R_{\oplus}$ making them compact objects with immense gravitational fields. As a result, elements in the atmospheres of WDs heavier than He settle into the star's core and out of sight (Paquette *et al.* 1986; Koester 2009). Despite their strong gravitational fields, up to 50% of WDs are 'polluted' and exhibit heavy elements in their atmospheres (Zuckerman *et al.* 2003, 2010; Koester *et al.* 2014). This pollution is exogenous to the star; these heavy elements originate from vaporized rocks, torn apart by the gravitational field of the WD (Debes & Sigurdsson 2002; Jura 2003). Some polluted WDs exhibit infrared excesses, evidencing surrounding debris disks (e.g. Jura *et al.* 2007). By observing polluted white dwarf stars, and measuring the abundances of the heavy elements in their atmospheres, one can constrain the cosmochemistry of the rocky bodies that previously orbited them.

Thus far, parent bodies accreting onto polluted white dwarf stars resemble rocky bodies in the Solar System (e.g. Jura & Young 2014). The material accreting onto the white dwarf stars in this work are chondritic or basaltic; these bodies are devoid of metal cores. Doyle *et al.* (2019) showed that oxygen fugacity (f_{O_2}), a specific geochemical parameter that characterizes the overall oxidation state of a rocky body, can be constrained using WD elemental abundance data.

2. Oxygen Fugacity

The partial pressure of O_2, oxygen fugacity, is a thermodynamic quantity that characterizes the level of oxidation in a system. Geochemists use f_{O_2} as a measure of the partial pressure of O_2 in non-ideal thermodynamic systems. Oxygen fugacity can be used to characterize the oxidation state of a system even where O_2 gas may never have existed, as long as a reaction between the constituents of the system and O_2 can be written and quantified thermodynamically. The equilibrium reaction between pure metallic iron (Fe) and pure wüstite (FeO) defines the reference f_{O_2} commonly used in cosmochemical studies. This so-called Iron-Wüstite (IW) reference reaction is

$$\mathrm{Fe} + \frac{1}{2}\mathrm{O}_2 \rightleftharpoons \mathrm{FeO}. \tag{2.1}$$

A simple thermodynamic expression relates the oxygen fugacity for any geochemical system containing oxidized and reduced iron to that of the IW reference:

$$0 = \Delta\hat{G}^0 + RT\ln\left(x_{\mathrm{FeO}}\right) - RT\ln\left(x_{\mathrm{Fe}}\right) - \frac{1}{2}RT\ln\left(f_{O_2}\right) \tag{2.2}$$

where $\Delta\hat{G}^0$ is the Gibb's free energy for the reaction in Equation 2.1 at standard state (1 bar, 298 K, pure Fe and FeO), x_{FeO} and x_{Fe} are mole fractions of FeO and Fe in their respective impure mineral phases, T is the temperature of interest and R is the ideal gas constant. Relating the oxygen fugacity of a rock to a reference reaction like Equation 2.1 results in cancellation of specific thermodynamic constants so that one can refer just to the difference in oxygen fugacity relative to the IW reference, ΔIW. In this case all that is required is the mole fraction of FeO in the rock ($x_{\mathrm{FeO}}^{\mathrm{rock}}$) and the mole fraction of Fe in the metal ($x_{\mathrm{Fe}}^{\mathrm{metal}}$), yielding:

$$\Delta\mathrm{IW} \equiv \log\left(f_{O_2}\right)_{\mathrm{rock}} - \log\left(f_{O_2}\right)_{\mathrm{IW}} = 2\log\left(\frac{x_{\mathrm{FeO}}^{\mathrm{rock}}}{x_{\mathrm{Fe}}^{\mathrm{metal}}}\right) \tag{2.3}$$

Following Doyle *et al.*, minerals comprising rocks in our solar system can be thought of as being composed of the oxides SiO_2, MgO, FeO, CaO and Al_2O_3. The relative proportions of these metal oxides reflect the compositions of the major minerals. The ability to measure all major rock-forming elements in a polluted WD affords the opportunity to use the abundances of FeO as a measures of the oxidation states of exoplanetary materials. Polluted WDs with quantifiable concentrations of O, Fe, Mg, Si, Ca and Al can be used to calculate oxygen fugacity, assuming there was at least a small amount of metal present during the formation of the body. By first assigning oxygen to Mg, Si, Al, and Ca to form these oxides, and then assigning the remaining oxygen to Fe, to form FeO, one can calculate the relative amount of oxidized Fe, as FeO, and assign any remaining Fe to metal, representing iron core material, if present. Measurement uncertainties for the polluted WDs are propagated using a Monte Carlo approach with an $n = 1$ bootstrap to obtain a frequency distribution of oxygen fugacities for each WD.

This use of FeO to estimate oxygen fugacities can be illustrated using Solar System bodies with known oxygen fugacities as examples. For instance, Mercury and Earth have very different intrinsic oxygen fugacities, as recorded at the time of core-mantle equilibration (e.g. Zolotov *et al.* 2013); Frost & McCammon (2008). This difference between Mercury and Earth is manifested by how much iron each body contains in its rock. Earth has about 8 wt. % FeO in its mantle rocks and those rocks produced by partial melting of the mantle (e.g., crustal basalt), whereas Mercury is estimated to have about 1 wt. % FeO in its rocks (Rubie *et al.* 2004; Nittler *et al.* 2018). This difference corresponds to a difference in intrinsic oxygen fugacity of 5 orders of magnitude, with Mercury having f_{O_2} values comparable to that of a solar gas, and Earth having an f_{O_2} 10^5 times greater than solar and closer to the IW reference defined by the reaction in Equation (2.1).

3. Oxygen Fugacity of Rocks Accreted by White Dwarfs

The method used to obtain ΔIW values for the rocky material accreted to WDs is detailed more thoroughly in Doyle *et al.* (2019). The method was validated using Solar

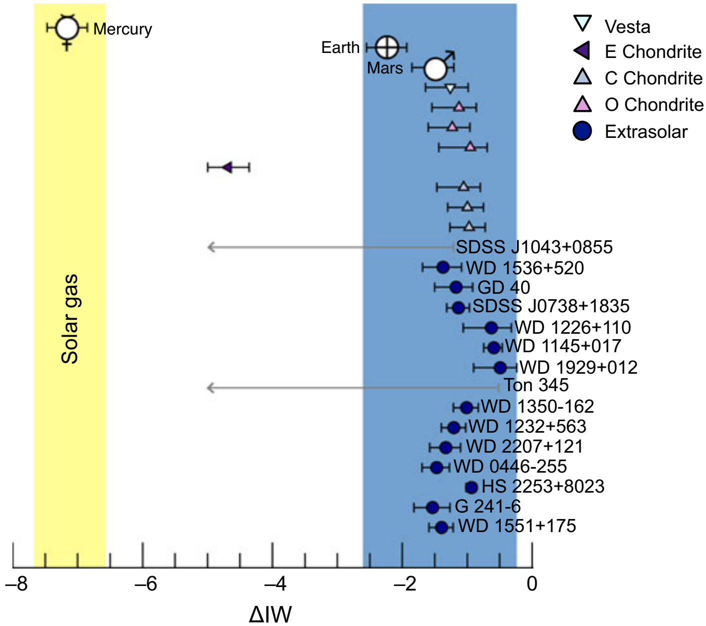

Figure 1. Oxygen fugacity values for rocky bodies accreting onto white dwarf stars. Recovered values for Solar System bodies are shown for comparison. WD abundance data from top to bottom: Melis & Dufour 2017; Farihi *et al.* 2016; Jura *et al.* 2012; Dufour *et al.* 2012; Gansicke *et al.* 2012; Xu *et al.* 2016; Gansicke *et al.* 2012; Swan *et al.* 2019; Xu *et al.* 2019; Wilson *et al.* 2015; Xu *et al.* 2019; Swan *et al.* 2019; Klein *et al.* 2011; Jura *et al.* 2012; Xu *et al.* 2019.

System rocks; the compositions of various Solar System bodies were converted into hypothetical polluted white dwarfs, as if the rocks from these bodies had accreted onto a WD, with typical WD measurement uncertainties. Doyle *et al.* recovered the known intrinsic oxygen fugacities for Mercury, Earth, Mars, Vesta and a range of chondritic bodies, including enstatite and CI chondrites. Figure 1 shows that the Solar System bodies span a range in ΔIW of ∼6 dex, which agrees with previous studies showing that Mercury and enstatite meteorites have oxygen fugacity values orders of magnitude lower than those for Earth, Mars, and other chondrite group meteorites (e.g. Cartier & Wood 2019). For the 15 WDs shown in Figure 1, the calculated ΔIW values for the accreted rocks are all similar to those of the oxidized bodies in the Solar System. When metallic iron is abundant, only an upper limit can be constrained for ΔIW, as shown for SDSS J1043+0855 and Ton 345, because the errors in estimating FeO concentrations become unwieldy.

4. Implications

Oxidation. The process that oxidized most rock-forming materials in the Solar System, relative to a hydrogen-rich gas of solar composition, also operated in these other planetary systems. One explanation is that this oxidation occurred early and involved the amount of water present in the disk at the time and place of rock formation (Monteux *et al.* 2018). Another explanation could be aqueous alteration of asteroidal parent bodies, occurring after rock formation but prior to assembly of planets. If the latter case is the correct explanation, then serpentinization, the process of converting anhydrous minerals into hydrous minerals and in so doing releasing H_2 gas, may be the primary oxidation process associated with terrestrial planet formation.

Habitability. Oxygen fugacity is a parameter that is as important as pressure and temperature in determining the dominant mineral assemblages present in planetary interiors.

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Along with bulk composition, mineral structure is an important factor in determining how heat is transported through a body, how much water exists in a planet's mantle, and the presence or absence of a magnetic field (Pearson *et al.* 2014; Frost *et al.* 2001; Frost & McCammon 2008; Elkins-Tanton & Seager 2008; Wood *et al.* 2006; Buffett 2000). Additionally, oxygen fugacity and mineral assemblage will play a part in determining what type of volcanism a planet will have, which has implications for the existence of plate tectonics and the composition of the planet's initial atmosphere (e.g. Kolzenburg *et al.* 2018; Schaefer & Fegley 2017). Indeed, many geophysical aspects that are thought to be important for habitability are at least in part determined by oxygen fugacity.

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