**INTRODUCTION**

We describe the development of thermodynamic equations of state for oceans in exoplanets, and application to their interior structure. Specifically, we consider ice-covered Earth-sized exoplanets that we term super-Europas and super-Ganymedes, a class of potentially habitable worlds that may be more abundant than Earth-like planets.

**Super-Europas and Super-Ganymedes:** Tidal heating could be significant in ocean-bearing worlds that orbit close to their parent M-dwarf stars, leading to the formation of subsurface oceans in watery Earth-sized planets outside the conventional "habitable zone", orbital range for Earth-like climate conditions [e.g., 1]. The catalogue of such worlds should grow starting in 2017, when the Transiting Exoplanet Survey (TESS) comes online (Fig. 2). Constraining the interior structure and processes in such worlds would lead to predictions of surface features observable by future observatories.

**Figure 1.** Earth-like planets covered in water are common around other stars, as shown in this plot of confirmed and candidate Kepler planets (contours are temperature in Kelvin). Future determination of the masses and radii of super-Earths, super-Ganymedes, and super-Europas will be strengthened by accurate constraints on their thermal and compositional evolution, provided by coupling new equations of state for fluids and minerals to mass-radius relationships, including cooler exoplanets (e.g., Sotin et al. 2007, Grasset et al. 2009, Fu et al. 2010) that will be increasingly important as new facilities such as TESS come on line.

**Figure 2.** Increasing number of exoplanets found by TESS. The increase is anticipated from future observatories.

Internal structure models for Earth-like exoplanets can be used to constrain compositions derived from observations of mass-radius (M-R) relationships [2-12]. Conversely, interior models can be used to infer M-R relationships when coupled with knowledge of surface temperature and composition, and composition of the host star. Assuming likely mineralogical compositions of the core, upper and lower mantle, and H2O-rich upper layer, thermodynamic equations of state—based on available laboratory measurements usually obtained in the context of Earth studies—allow the determination of pressure, temperature, density, and phase boundaries as a function of depth.

Likely mineralogical compositions have included Mg,Fe perovskites and olivine, along with Mg,Fe ringwoodite in the lower regions [7]. Mineral physics studies for Earth have explored the role of Ca and Al in perovskites in Earth’s mantle, and the presence of dense phases such as post-perovskite in the very lowest part of the mantle [13, 14]; the latter has been considered as an important phase in super-Earths [5, 15, 16]. Refractory phases are acknowledged as potentially having a significant presence in super-Earths [17,18], but realistic equations of state have not been incorporated into models of their internal structure.

The incorporation of H2O is least certain among the materials involved, and can have the strongest influence on the M-R relationship [7]. Interaction between liquids and solids is intimately connected with a planet’s internal structure, through its influence on the planet’s mineralogical and thermal state through time. Where present, liquid water will have a key role in thermal transport on exoplanets [19]. Convection, in ice, rock, or liquid, depends critically on the presence of a cool boundary layer and low material viscosity [8]. Plate tectonics mediated by liquids may be key to efficient mantle convection in exoplanets [20]. Direct contact between liquids and rock is implicated in maintaining plate tectonics on Earth [e.g. 21], but such interactions have been assumed to be limited in larger bodies and icy moons of the solar system by dense high-pressure ices [e.g., 8].

**Geophysical Inverse Theory Used to Advance Aqueous Geochemistry:** Interactions between aqueous solutions and rocks extending from the surface and through the deep mantle control the state and evolution of planetary interiors. Accurate representation of the fluid chemical energy as a function of pressure, tem-
temperature and composition over a wide range of conditions is a prerequisite in understanding phase equilibria and solubilities in multicomponent systems. End-member thermodynamic properties of water (densities, specific heats, sound speeds, and more) have been extensively explored in a regime below about 100 MPa and an available complex formulation for the Helmholtz free energy [22] accurately represents these data and a smaller number of measurements extending to 1 GPa. However, this parameterization systematically misfits higher pressure data and is not easily adjusted to provide a better description [23]. To address these points, we developed a flexible framework for acquiring and describing Gibbs’ free energy of water and aqueous solutions. Using local basis functions, the thermodynamic state surface can be adjusted to account for improved experimental constraints or results in new regimes of pressure and temperature (Fig. 2).

**Application of New Equations of State to Exoplanet Interiors:** Based on our experimental work on pure water, MgSO$_4$(aq), Na$_2$SO$_4$(aq), and ammonia-water mixtures, we are constructing user-friendly data sets that can be used for geophysical and geochemical calculations. In this presentation we will describe possible ocean and mantle structures in ice-covered exoplanets, including the potential for buoyant high-pressure ices [25] and the role of stellar composition in determining the occurrence of solid-state convection in rocky and icy mantles.

**References:**

**Figure 2.** Pressure and temperature profiles in the upper mantles of selected objects, below putative or known H$_2$O-rich layers. In each case, the plot of pressure (in MPa) versus temperature (in °C) begins at the estimated depth of the seafloor, with the overlying ocean assumed to be at a roughly constant temperature. We are constructing self-consistent thermodynamic frameworks appropriate for the extended pressure and temperature conditions occurring on other worlds.