

# Thermodynamic Equations of State for Aqueous Ammonia and Sodium Chloride Applied to Exoplanet Oceans and Interiors



Steve Vance<sup>1,2\*</sup>, J. Michael Brown<sup>2</sup>, Mathieu Choukroun<sup>1</sup>, Olivier Bollengier<sup>2</sup>, Baptiste Journaux<sup>3</sup>, Christophe Sotin<sup>1</sup>, and R. Barnes<sup>4</sup>

\*svance@jpl.nasa.gov

<sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology

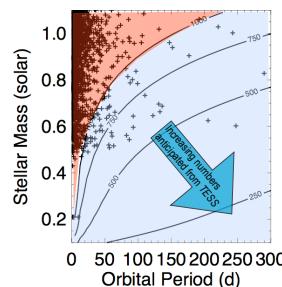
<sup>2</sup>Department of Earth and Space Sciences, University of Washington, Seattle

<sup>3</sup>Laboratoire de Glaciologie et Géophysique de l'Environnement, Université Joseph Fourier, Grenoble, France

<sup>4</sup>Department of Astronomy, University of Washington, Seattle

## SUMMARY

- Fluid-rock interactions in super Earth oceans are regarded as limited by negatively buoyant high pressure ices V, VI, VII, and VIII.
- Analogous assumption made for large icy worlds Ganymede and Titan: ocean depths up to 800 km create >GPa pressures (>10kbar). Applying accurate fluid thermodynamics to planetary interiors challenges these assumptions.
- Increased density in highly saline oceans implies possible oceans perched under and between high pressure ices.
- In some model oceans, high-pressure ices become buoyant, implying frazil-like upward snows, interlayered liquids and fluids in direct contact with rock.



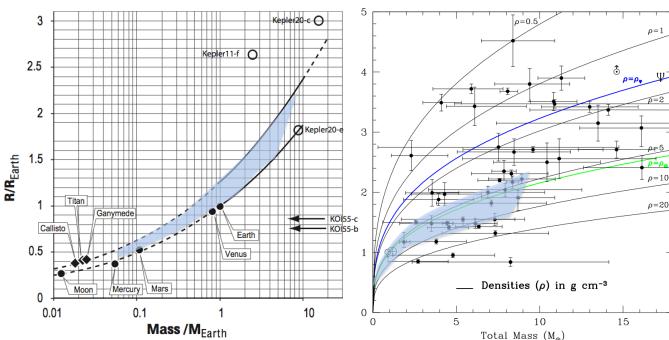
### 1. Confirmed and candidate

Kepler planets with  $R < 2.5 R_{\oplus}$ .  
→ Watery Earth-like planets are probably common around other stars.  
(contours: temperature in Kelvin).

More small, cool worlds will be discovered as facilities such as TESS come into operation [1].

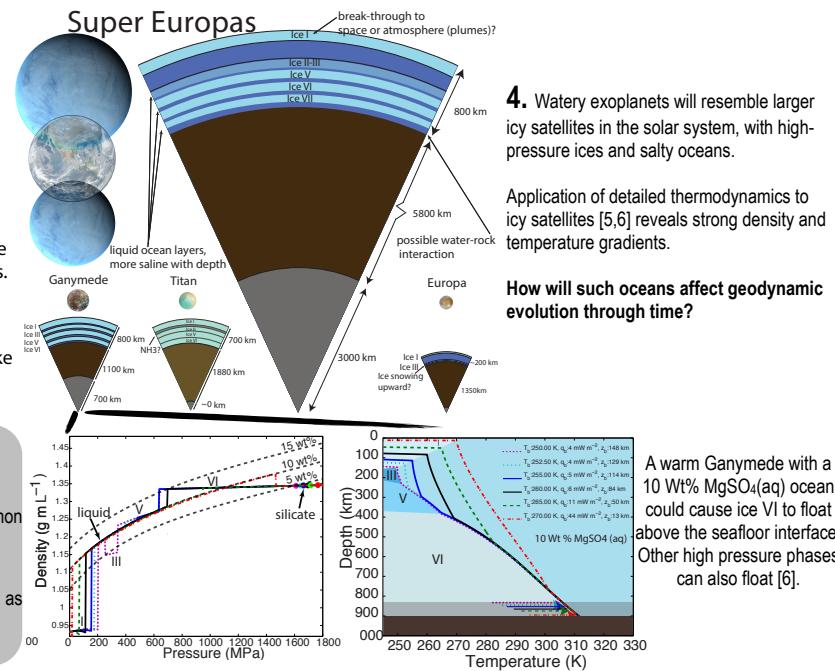
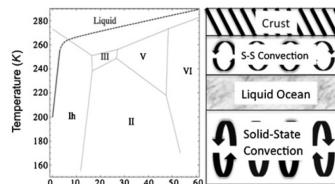
### 2. Mass-radius, planet density vs composition, etc., provide information about internal structure related to habitability.

Potentially habitable super Europas are notionally in the shaded regions.



530 model planets [2].  
curves separate wet (upper) and dry (lower) worlds.  
Jupiter's moon Europa at the same position as the Moon.

### 3. Interior models for $5 M_{\oplus}$ water planets [4], with water oceans with $\text{NH}_3$ neglects effects of dissolved species (salts).



4. Watery exoplanets will resemble larger icy satellites in the solar system, with high-pressure ices and salty oceans.

Application of detailed thermodynamics to icy satellites [5,6] reveals strong density and temperature gradients.

### How will such oceans affect geodynamic evolution through time?

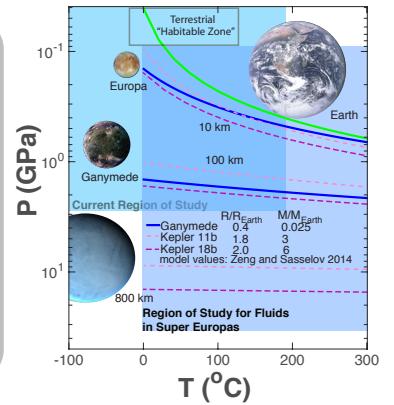
A warm Ganymede with a 10 Wt%  $\text{MgSO}_4(\text{aq})$  ocean could cause ice VI to float above the seafloor interface, Other high pressure phases can also float [6].

### 5. Pressures in exoplanet oceans span the multi-GPa range of pressures where liquids are possible.

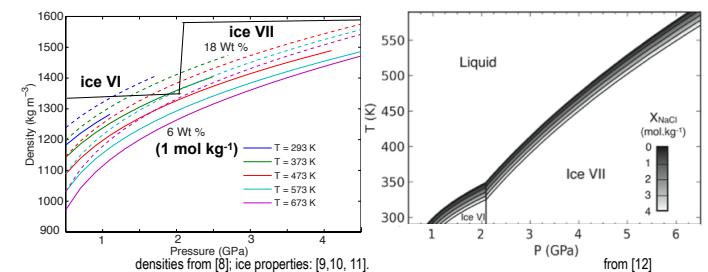
Pressure (GPa), temperature (°C) profiles in upper mantles of selected objects [as per Ref. 7], beginning at presumed seafloor depth.

Overlying ocean assumed at a constant temperature.

Known exoplanets, albeit very hot ones, modeled as super Europas with seafloor depths like Earth's (10 km), Europa's (100 km), and Ganymede's (800 km); [6].



### 6. Recent EOS and phase measurements for $\text{NaCl}(\text{aq})$ indicate ice VII floats at $P > 5 \text{ GPa}$ .

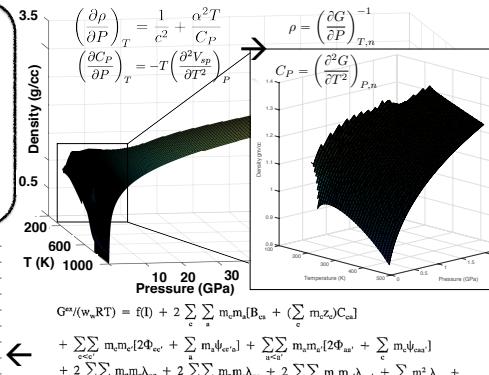
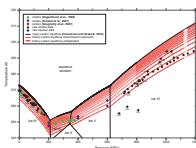


## REFERENCES

- [1] Ricker, G. R., et al. (2014). *SPIE Astronomical Telescopes+ Instrumentation*, 914320–914320.
- [2] Baraffe, I., et al. (2014). arXiv preprint arXiv:1401.4738.
- [3] Howe, A. R., et al. (2014). *Astrophys. J.*, 787(2):173.
- [4] Fu, R., et al. (2010). *Astrophys. J.*, 708:1326.
- [5] Vance S. and Brown J. M. (2013) *Geochim. Cosmochim. Acta*, 90, 1151–1154.
- [6] Vance S. et al. (2014) *Plan. Space Sci* 96, 62–70.
- [7] Vance et al. (2007) *Astrobiology*, 7, 987–1005.
- [8] Mantegazza, D., et al. (2013). *Geochim. Cosmochim. Acta*, 121:263–290.
- [9] Reimers, J. and Watts, R. (1984). *Chem. Phys.*, 91(2):201–223.
- [10] Vega, C., et al. (2005). *Phys. Chem. Chem. Phys.*, 7(7):1450–1456.
- [11] Choukroun M. and Grasset O. (2010) *J. Chem. Phys.*, 133, 144, 502.
- [12] Journaux, B., et al. (2013). *Icarus*, 226:355–363.
- [13] Vance S. and Brown J. M. (2010) *JASA* 127, 174–180.
- [14] Abramson, E. and Brown, J. (2004). *Geochim. Cosmochim. Acta*, 68(8):1827–1835
- [15] Pitzer, K. (1991) CRC Press.

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Gibbs free energies of  $\text{MgSO}_4$  allow computation of ice equilibrium under super Earth pressures. (Bollengier et al., in prep)



7. Modern computer processing allows us to apply geophysical methods of regularization to construct optimized "local" fits of thermodynamic properties that easily accommodate new data.

We constructed Gibbs free energies for water at relevant pressures and temperatures [13, 14, Brown et al., in prep].

We are using G to develop general thermodynamics of aqueous solutions:

Pitzer formulation[15]  $G = G_{\text{water}} + G^{\text{ex}}$