Pressure Dependence of Liquidus Temperatures for Methanol-Water Mixtures with Application to Titan

Zachary Bartholet

Introduction

The experiment studied the liquidus temperature of methanol-water solutions at various pressures and concentrations. The liquidus temperature of a solution is the lowest temperature where the solution is still entirely liquid. Because methanol acts as an antifreeze, as methanol is added to the solution its liquidus temperature decreases. The experiment was performed in order to get a better understanding of the subsurface oceans of icy moons, particularly Titan.

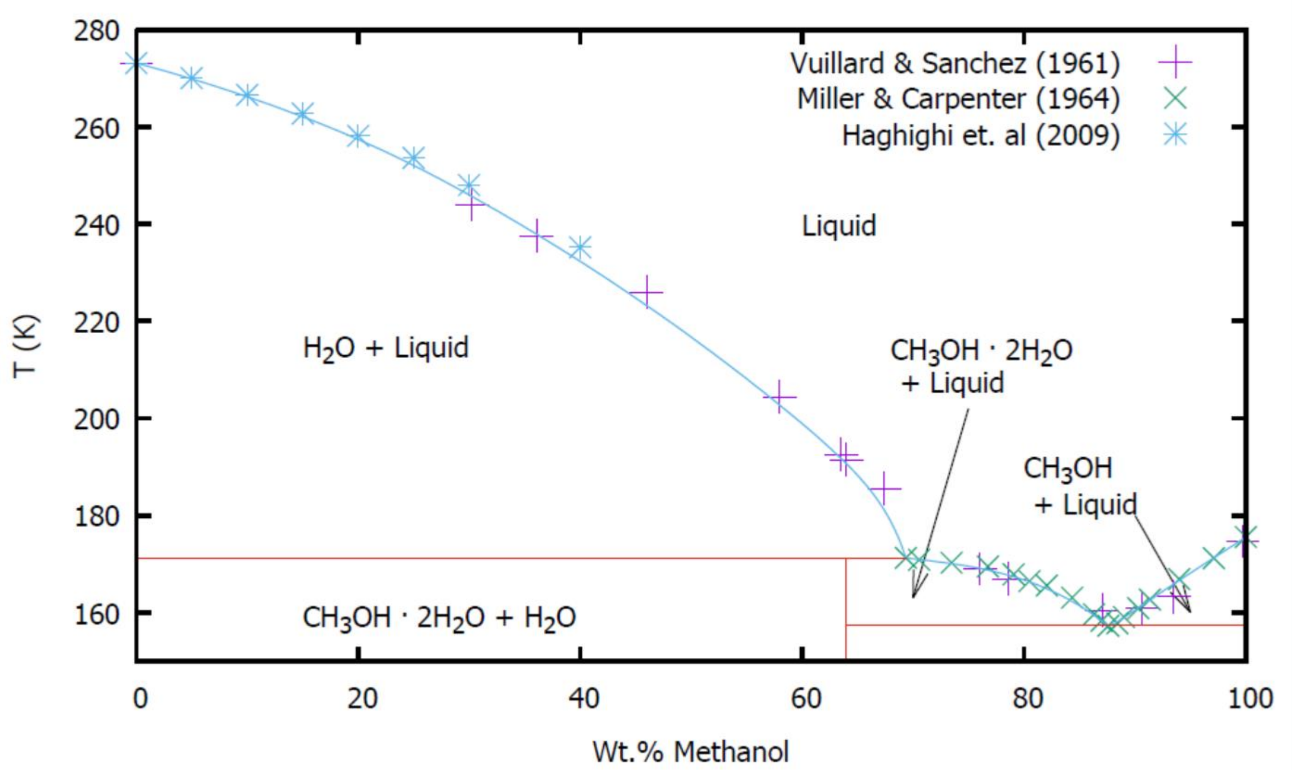

Fig. 1. Graph showing the liquidus temperatures of solutions with different concentrations of methanol. The curves were fit to data gathered from various sources.

Background

Analysis from the *Huygens* probe and gravity measurements suggest that there is a liquid ocean beneath Titan's outer shell of ice Ih, the type of ice common on Earth's surface and which is less dense than water. There is also a significant amount of methane in Titan's atmosphere that seems to be continuously replenished from Titan's interior suggesting a multilayered structure like the one shown below. Below the subsurface ocean, the pressures are great enough to create another layer of ice, this time ice VI, which is more dense than water. Some of the most likely candidates for impurities in Titan's ocean are ammonia and methanol, both of which act as antifreeze compounds. Since it is likely Titan's ocean contains methanol, it would be good for experiments to explore the phase diagram of methanol-water solutions.

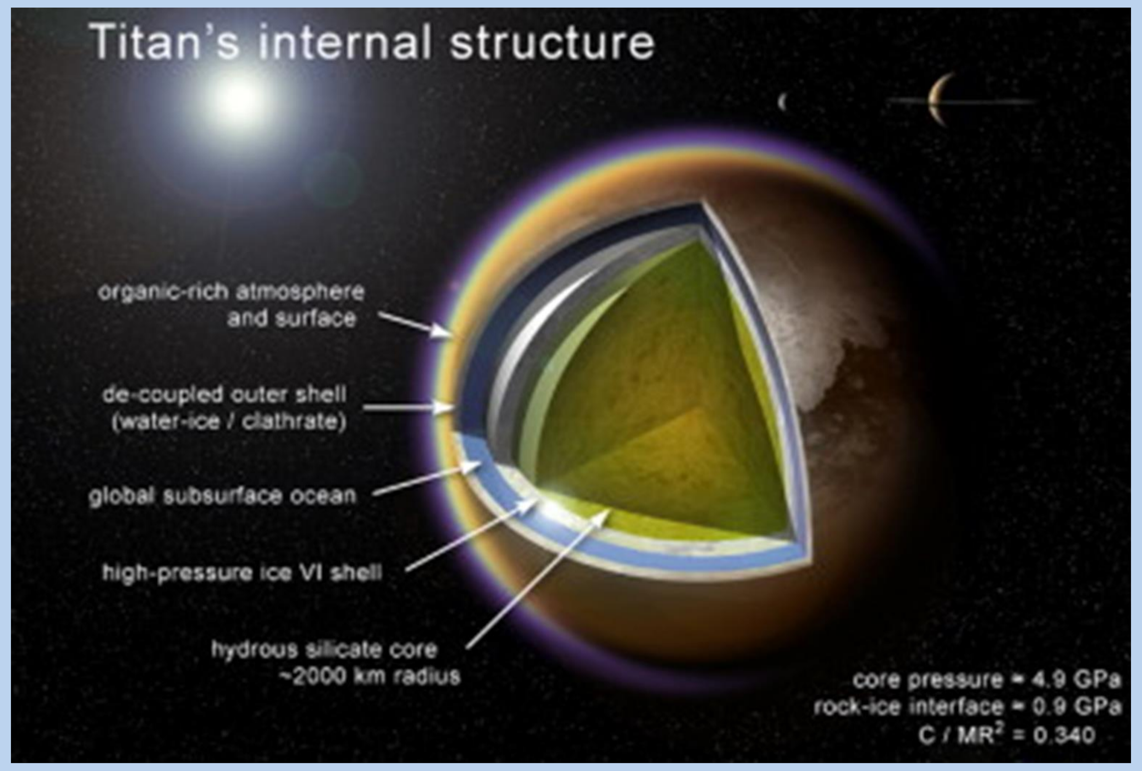

Fig. 2. Possible model of fully differentiated Titan with surface layer of ice Ih and subsurface ocean.

Apparatus

The apparatus used for this experiment consists of a pressure cell submerged in a bath of ethanol with a chiller to control the temperature, a high pressure pump used to change the pressure of the sample, an optical system, and numerous probes to find various temperatures of different parts of the system. Volume is measured through a transducer which records the voltage received from a magnet suspended between liquid mercury and pump fluid. The height of the magnet changes the recorded voltage, which is roughly proportional to volume.

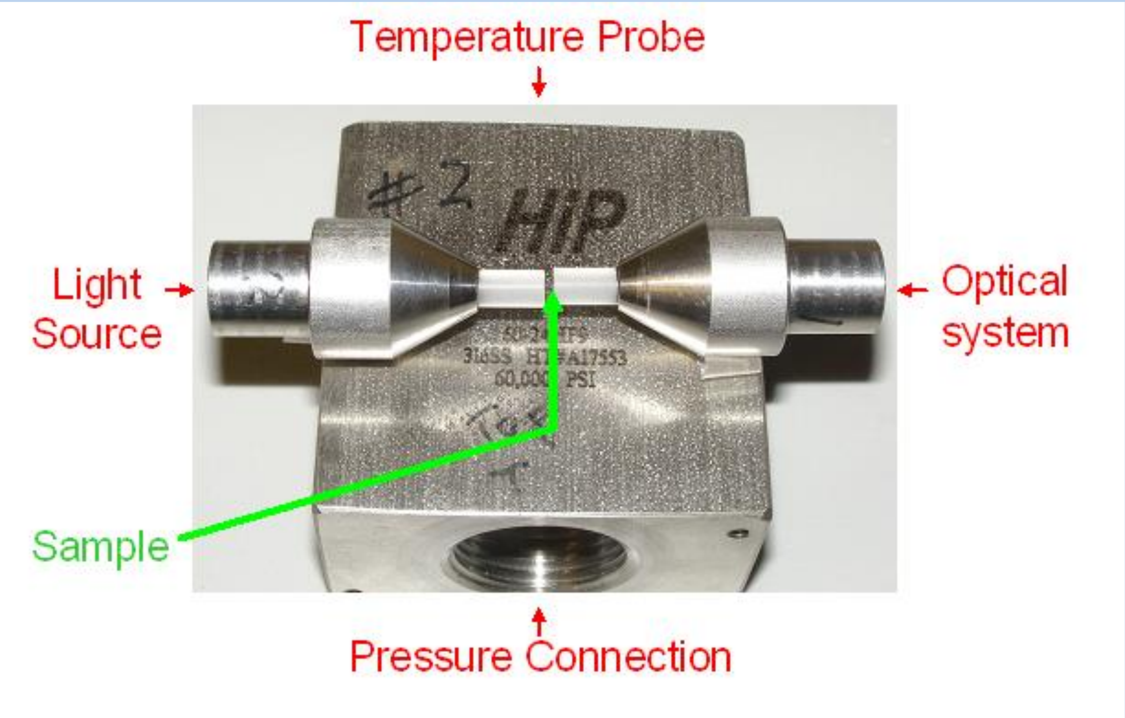

Fig. 3. Picture of the cross used to store sample. On all four sides of the cross there are ports used to connect it to the rest of the apparatus. The top port contains the temperature probe, the bottom port contains the pressure connection. The left port contains the light source (probe shown) and the right port contains the optical system (probe shown). The sample lies between two sapphire crystal windows, allowing a camera to view the sample.

Method

A typical run is shown as a chart of transducer voltage vs temperature. We started by pressurizing to 264.5MPa at a temperature of 255.72K to keep the sample a homogenous liquid (point a). Then, we began cooling until the sample rapidly froze at point b and crystalized accompanied by a sharp decrease in voltage and pressure (indicating the sample was ice III or ice V) and appearance of ice in the camera. The sample continued freezing until its pressure was 251.8MPa and its temperature was 237.02K (point c). The sample was then continuously warmed until it melted and a liquidus curve was received(point d). The sample continued warming to get a nice warming curve until the run was stopped at point e.

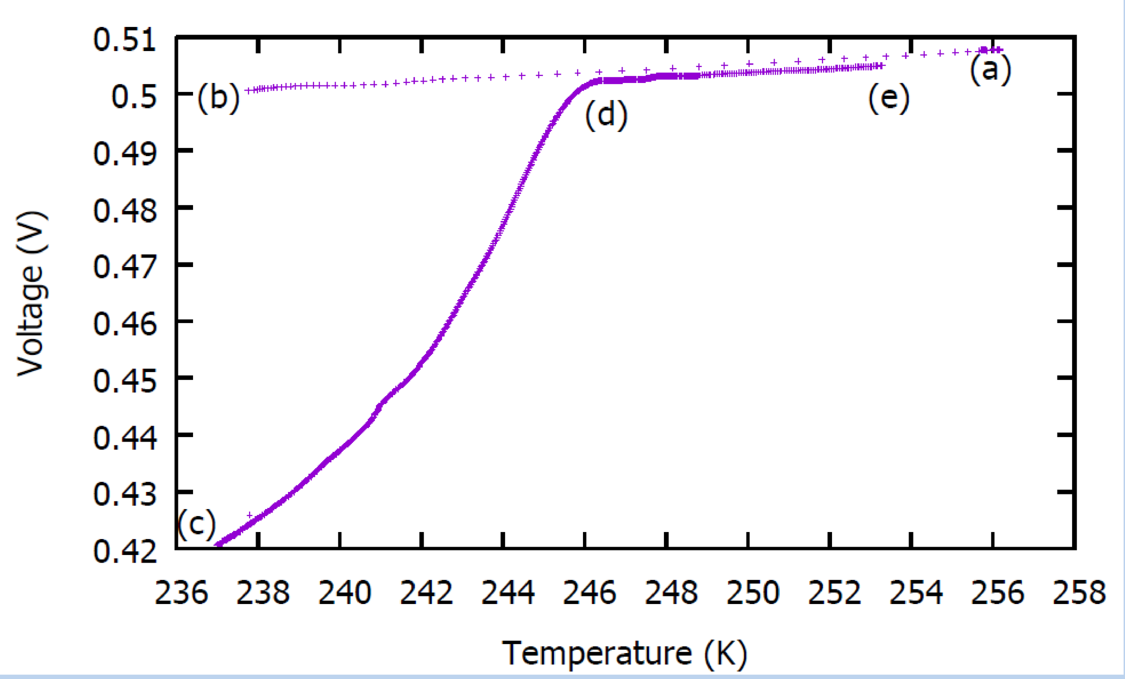

Fig. 4. Results for 265MPa. The liquidus temperature was 245.9K.

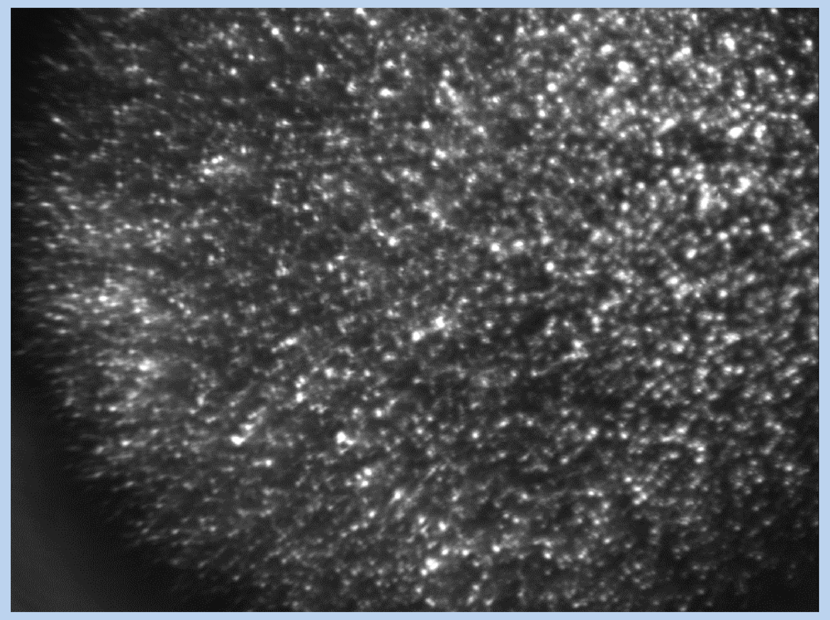

Fig. 5. Picture of the sample taken right after it froze at point c.

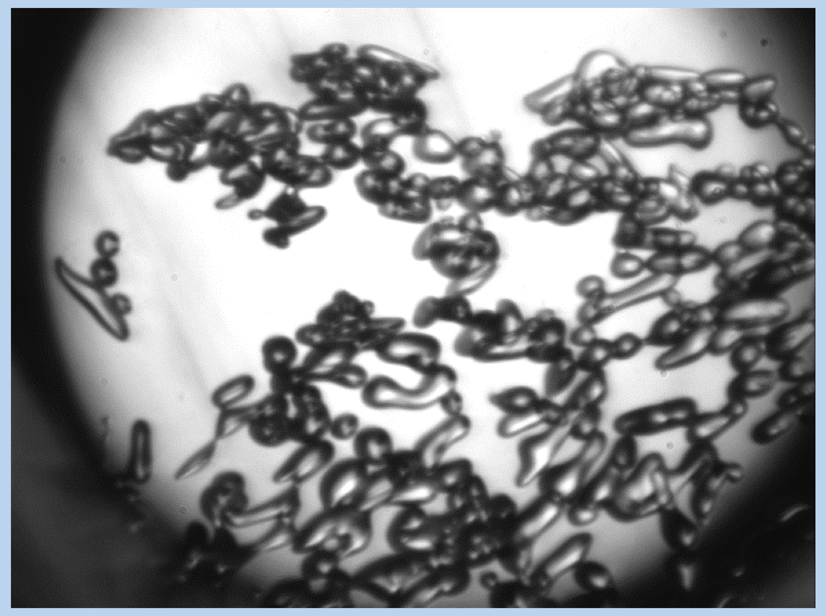

Fig. 6. Picture taken as the sample was melting, between points c and d. The crystals are falling downwards indicating that they are denser than water.

Results

After using the data to make a graph of Voltage vs Temperature, a Mathematica notebook was used to extend both the melting curve and the liquidus curve. Where the two lines met is where the liquidus temperature was estimated to be. Then, looking at the data, the pressure corresponding to this liquidus temperature was found. Data on the liquidus temperature at different pressures was taken for samples containing 4.9%, 9.9%, 33.8%, and 75% methanol.

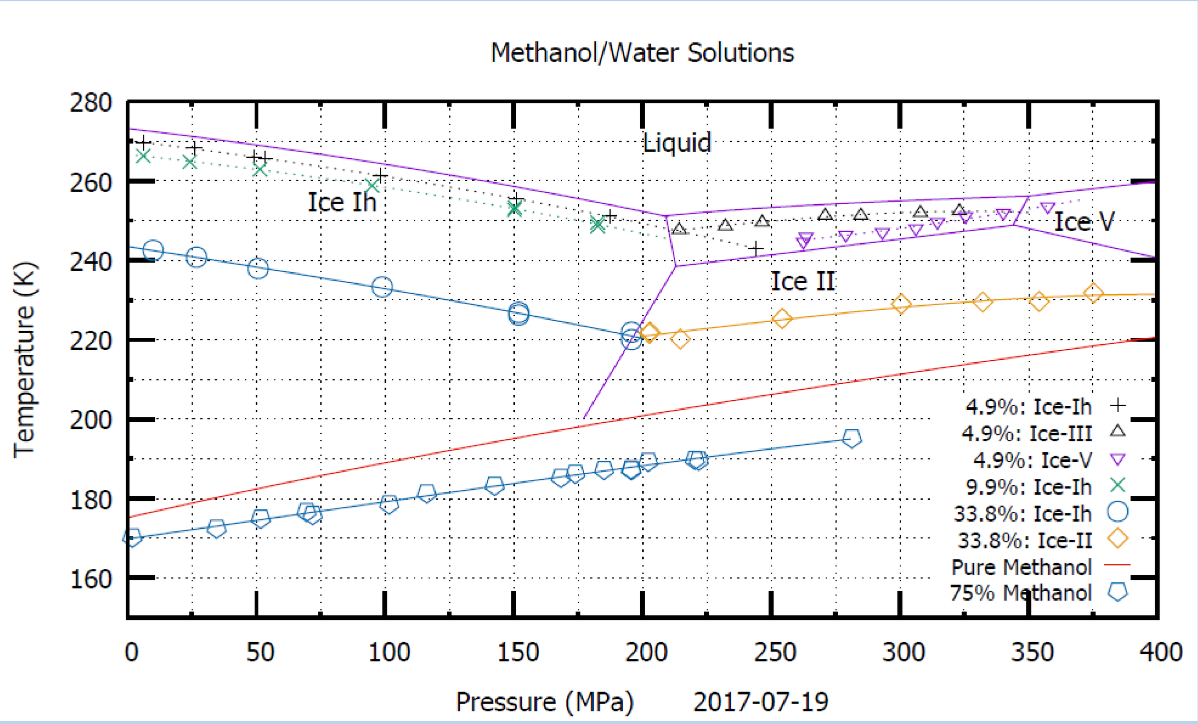

Fig. 7. Graph of the liquidus temperatures at various pressures of different methanol-water solutions with curves fit to the points.

To verify the concentrations, we compared the results at atmospheric pressure with the data in fig. 1. By fitting a curve to the liquidus points we measured pressures we were able to estimate the liquidus point at atmospheric pressure. Using that, we were able to plug it into the wt. % Methanol vs Liquidus Temperature curve and find the concentration of the sample. Using this method, we were able to find out that the concentrations for the samples were 4.9%, 9.9%, 33.8%, and 75% as shown in Fig. 7.

In the 4.9% sample, shown in more detail in Fig. 8., we observed three different states. The black crosses show the liquidus points of ice Ih, which is less dense than water. Therefore, as the pressure increased the liquidus temperature decreased. The black cross at 244.4 MPa is metastable ice Ih and extends into the ice III regime. The blue triangles are ice III which is more dense than water. Therefore, as the pressure increases, the liquidus temperature increases as well. The red triangles are the liquidus points of ice V which, with the exception of the point at 357.4 MPa, are all metastable.

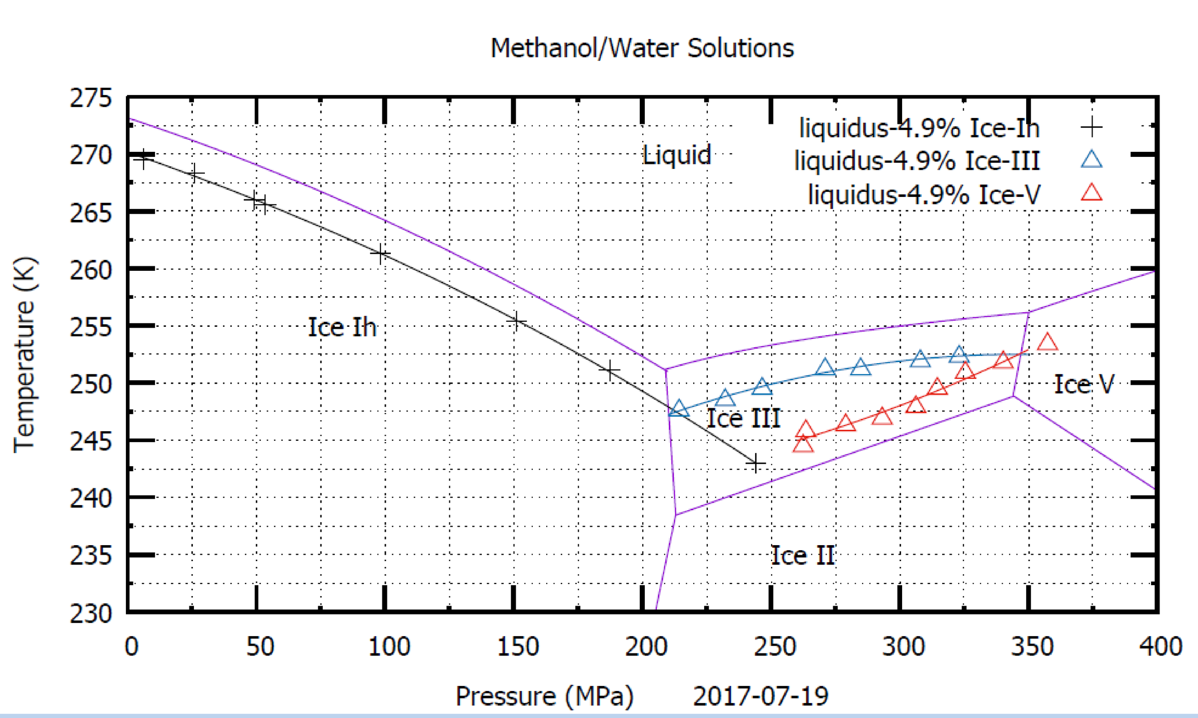

Fig. 8. Graph of the liquidus points of the 4.9% sample.

Conclusion

In the experiment, we observed methanol-water solutions in liquid, ice Ih, ice III, ice V, and ice II phases. We also created metastable ice Ih and ice V in the 4.9% methanol water solution. A metastable phase is one which appears outside of its normal range. Overall, methanol is a reasonable impurity to include in the models of the oceans of Titan and Enceladus, and since the properties of the icy shells and oceans of these planets depend on temperature, studying the liquidus points of methanol-water solutions should help further the understanding of the two moons.

References

Deschamps, F., O. Mousis, C. Sanchez-Valle, and J. I. Lunine (2010). Fortes, A.D. (2012). Haghighi, H., A. Chapoy, R. Burgess, S. Mazloum, and B. Tohidi (2009). Miller, G. A., and D. K. Carpenter (1964). Vuillard, G., and M. Sanchez 1961).