Nuffield Report

The behaviour of water molecules in the Shackleton crater

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Abstract

In this report I will look at why gases behave strangely at extremely low temperatures, how water molecules are able to attach to the inside of a lunar crater through cryocondensation. I will then go onto examine the different structures of ice I and the property of proton ordering. Next, I will examine the different forms of water isotopes and the scientific importance of their discovery on the moon. Finally, I shall evaluate my findings and adapt them into advice for the lunar mission one project, such as how they should interact with their lunar water samples once obtained.

1) Introduction

For my work experience I was given a placement with lunar mission one – a science and space exploration project that intends to send a probe to the Shackleton crater (located at the south pole of the moon) where it will drill 100 meters into the lunar mantle for geological samples. The probe will also see whether the environment of the south pole is suitable for a possible future manned base by examining the environment of the south pole and identifying any potential resources. Lastly the probe will place a time capsule at the south pole that would encapsulate humanity and could survive for a billion years.

For my placement with lunar mission one I was allowed to select a research topic relevant to the project and then carry out a presentation on my topic to members of the project. I quickly decided on researching a chemistry-relevant project and found my attention drawn to the Shackleton crater itself, which contained a considerable amount of frozen water. This fascinated me as it was one of the few places on the moon's surface where water could be found and I wanted to find out why water was only able to exist on the surface inside this type of crater.

The lunar mission one probe does intend to also collect water samples from the Shackleton crater so I would also try to find a way to take my research and adapt it into useful advice for the project.

2) Methodology

For researching my project, I started by getting in contact with Paul Bennett to request some further details about the crater’s environment so that I could look up studies which examined water molecules under these conditions. Paul suggested I look at cryopumping and the ideal gas law as these both fit into the same conditions and he was kind enough to help me find two research papers for me to read. Once I had begun reading these papers I decided to look into certain areas which were mentioned briefly in the paper but I knew would play a larger role in my context for instance, physisorption and chemisorption. For my own research techniques, I would look up specific topics on Google to find relevant sites and occasionally scientific papers that would contain some useful paragraphs that I could make notes from. However, since random websites on the internet are not always trustworthy I would often use multiple sites for a single topic, to ensure accuracy.

3) Results

Before I approach how water in the Shackleton crater behaves I will explain the chemistry behind certain characteristics of water molecules and their properties which I can then reference further on so as to explain the points I will make on what to expect from water in the Shackleton crater.

3.1.1) The Ideal Gas Equation

The ideal gas equation states that an ideal gas’ volume multiplied by its pressure is equal to the number of moles multiplied by the gas constant multiplied by the temperature ($PV=nRT$) however in reality, gases tend to deviate from this equation. Usually the deviation is so small it hardly matters, however gases at higher pressures and lower temperatures tend to deviate to a much larger extent. This is due to the fact that the ideal gas equation doesn’t take into account:

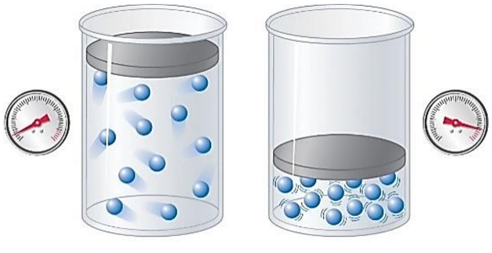
- The volume of the molecules[1]
- The intermolecular forces between the molecules[1]

Moreover, whilst this does only effect the equation slightly for the majority of gases it simply cannot be applied to gases at higher pressures and lower temperatures as it is under those conditions that these two factors have the most effect.

3.1.2) Volume

The volume that is calculated from the ideal gas equation is always lower than what it would be in reality. This is due to the fact that the gas molecules actually have minuscule volumes that are quantifiable but, because these volumes are so small the ideal gas equation simply considers the molecules to have no volume. Instead the equation uses the volume of the container as a measurement. This incorrect measurement becomes most noticeable when the gas is

Fig. 1

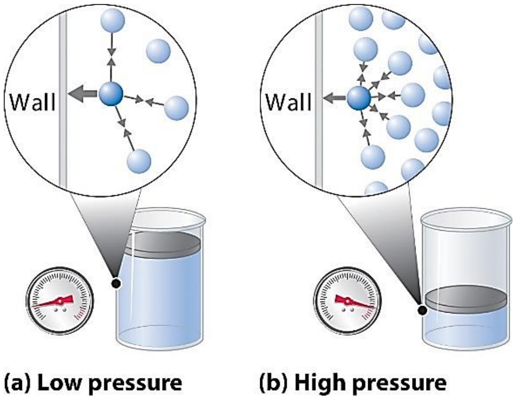


(a) Low pressure **(b) High pressure**

under extremely high pressure as this causes the molecules to be closer together and as a result, the volume occupied by the molecules of the container is a much more significant fraction and so real gases are much less compressible than ideal gases.[1]

3.1.3) Pressure

Fig. 2



The pressure that is calculated from the ideal gas equation is always higher than it would be in reality. This is because in the ideal gas equation, gases are assumed to bounce off one another with perfectly elastic collisions; when in reality intermolecular attractions and repulsions are occurring constantly. What happens is that the intermolecular attractions cause the molecules to travel towards each other rather than just randomly moving around, as the ideal gas equation also assumes, and so the molecules tend to travel inward which in turn, causes the number of collisions with the container wall to decrease slightly which genuinely lowers the pressure. These intermolecular forces have a more noticeable effect when the intermolecular distances are shorter (i.e. the molecules are closer together) which is at higher pressures and lower temperatures.[1]

3.1.4) The van der Waals equation

These anomalies are disastrous to the P x V side of the equation as the non-zero molecular volume causes it to increase to a considerable extent at higher pressures, and the intermolecular forces cause it to decrease, especially at lower temperatures (although increasing the pressure does effect both the volume and the intermolecular forces, it has a stronger effect on the non-zero molecular volume and so increasing the pressure increases the P x V). This is obviously an issue as it makes the ideal gas equation effectively useless in certain conditions and so some changes need to be made to improve the accuracy, these changes were made by Johannes van der Waals who realised that the equation needed to be specifically altered for each molecule as each molecule would have a unique volume and structure that would cause intermolecular forces to occur. So he designed the van der Waals equation:

$$\left[P + a\left(\frac{n}{V}\right)^2\right]\left(\frac{V}{n} - b\right) = RT$$

a and *b* are empirical constants which are unique for each gas, *a* provides a value for intermolecular forces whilst *b* provides a value for the molecules volume of one mole of the molecule.[1]

3.1.5) Liquefaction of Gases

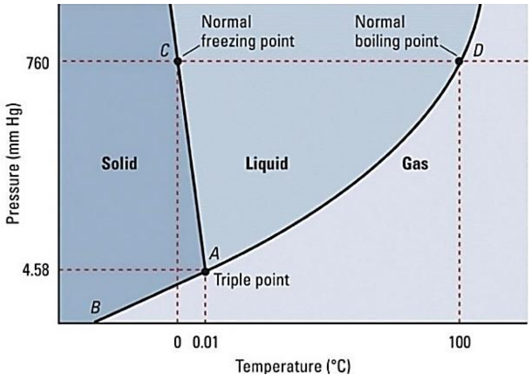
Liquefaction of gases is the condensation of gases, which is completely unanticipated by the kinetic molecular theory of gases and the ideal gas law. Both the theory and the law imply that when a gas is under high pressure and/or low temperatures it will behave like a dense/cold gas but instead the gas will condense to become a liquid. The gas condenses because its particle no longer possesses enough kinetic energy to overcome the intermolecular attractions. Each gas liquefies under different conditions, according to the volume and structure of the molecules, but in general molecules with larger *a* coefficients (from the van der Waals equation) are easier to liquefy as this means they have stronger intermolecular attractions.

The actual liquids formed from liquefaction are called cryogenic liquids and these liquids are always formed due to the environment having a low temperature not a high pressure.[1]

3.2) Phase factors of Water

Pressure and temperature are the main factors of determining the state the water is in; eg, high temperatures favour gas, low temperatures favour solid and high pressure favours liquid slightly more than solid, low pressure favours gas. Water is at its most unstable at the triple point, this is the point where solid, liquid and gas phase overlap as the favoured state.[2]

Fig. 3



3.3.1) Cryocondensation

For this process to be carried out; the surface must be extremely cold as the temperature alters the saturation pressure which must equal to, or below, the vacuum pressure.

During cryocondensation, layers of condensate form via crystal growth out of the gas phase, this occurs over a series of stages:

1. The cold surface cools the surrounding environment so any gas particles nearby will begin to lose their kinetic energy. The gas particles are also drawn to the cold surface as it has a larger mass.

2. Van der Waals and other intermolecular forces occur between the surface and the particle and since the particle has a lower kinetic energy these intermolecular forces have a stronger effect so that once the particle is close enough it becomes attached to the surface; through adhesion.

3. The gas particle undergoes deposition once enough kinetic energy is lost (deposition is the phase transformation from gas straight to solid).

4. Other gas particles impinge on the surface, but some will form a bond with the first particle rather than attach to the surface itself. This means that the first particle has become a growth site for a crystal lattice.

5. Over time, an equilibrium is established between the number of molecules in the gas phase and the number of molecules in the condensate layers.[3]

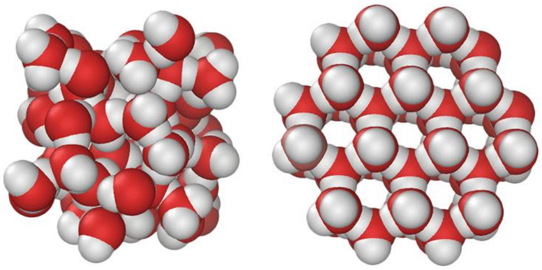
3.3.2) Physisorption and Chemisorption

When a particle becomes attached to the cold surface through weak intermolecular forces it is referred to as physisorption but if the surface and the particle happen to be able to form a chemical bond due to their specific structures, it is called chemisorption.[4] There are several differences between these two processes they are shown below:

Physisorption	Chemisorption
bond energy = 5 – 40 kJ mol^{-1}	bond energy = 40 – 800 kJ mol^{-1}
non-surface specific	surface specific
forms multiple layers	can only form a single layer
Reversible process	Irreversible process
does not require any activation energy	requires activation energy
occurrences of physisorption decrease as temperature increases	occurrences of chemisorption increase as temperature increases

3.4.1) Ice structure

When water molecules are cooled to a low enough temperature they will freeze which is the transition into the solid phase, the frozen water will form crystal lattices (aka ice) although to fully explain how this works it is useful to compare the structures of ice and liquid water. In liquid water hydrogen bonds occur between the partially positively charged hydrogen atoms and the lone pairs of electrons found in the oxygen atom (which have a partial negative charge) creating a strong attraction, out of all the intermolecular forces hydrogen bonds are strongest and they are responsible for many of water’s unusual properties (eg. surface tension) however, these hydrogen bonds are temporary in the liquid and gas phases and are constantly breaking and reforming. With ice this is not the same because the molecules have a lot less kinetic energy and so the hydrogen bonds formed are permanent, also in the solid phase water molecules arrange themselves at specific orientations so that as many hydrogen bonds can form with their neighbouring molecules as possible although, this causes the water molecules to be slightly further apart in ice than they are in water which means that ice is less dense than water.[5]



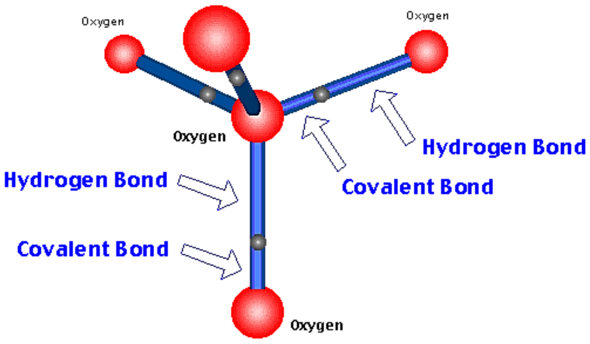
Liquid water

Frozen water

Fig. 4

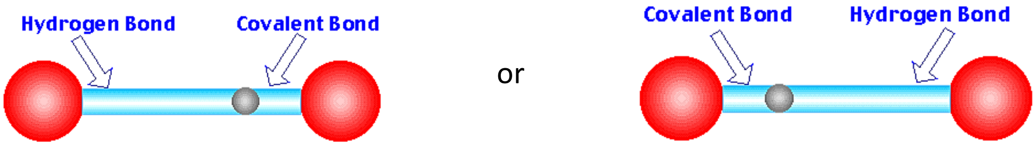
3.4.2) Hydrogen and Covalent bonds in Ice

Fig. 5



The hydrogen bonds that form in ice are almost perfectly orientated so that they are as far away from the covalent bonds on the hydrogen and oxygen atoms as possible which leads to a surprising effect; four water molecules will bond together in a tetrahedral format. The reason this happens is because of the "ice rules" which state that "each oxygen atom must have two nearest neighbor hydrogen atoms (forming a water molecule) and each oxygen – oxygen bond must be occupied by exactly one hydrogen atom."[12] This tetrahedral arrangement of water molecules gives ice a stable structure that requires a relatively large amount of energy to break apart. Furthermore, the hydrogen bond and the covalent bond between the oxygen atoms can be arranged in two different ways:

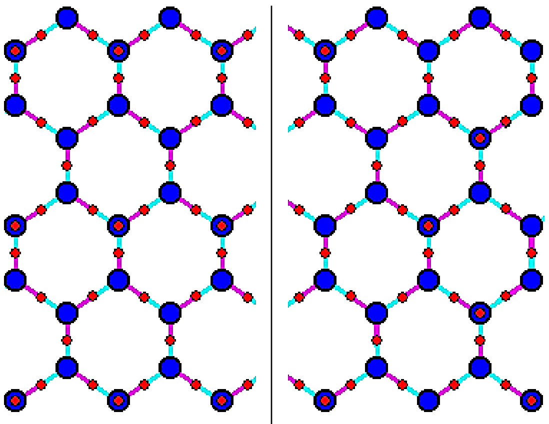
Fig. 6



This allows for the hydrogen atoms in the ice to move around the oxygen atom they are bonded to which, in turn, allows ice to conduct electricity, a trait which is very rare amongst covalently bonded molecules.[2]

3.4.3) Proton Ordering

Fig. 7

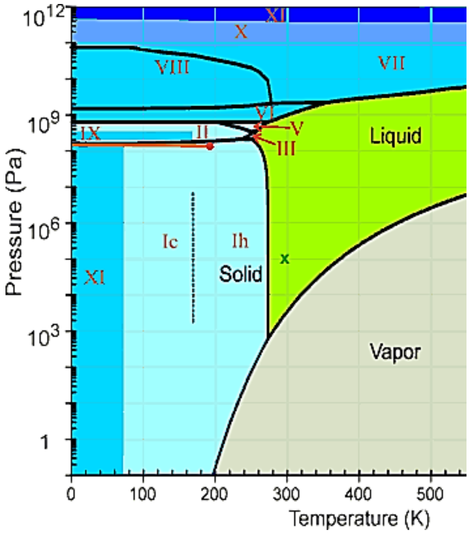


proton-ordered ice | proton-disordered ice

Proton ordered crystal lattices have the most stable arrangement of molecules in a structure but, such a small amount of energy is needed to break up proton ordering that it can rarely be found above around -100 °C. In water proton ordering takes the form of whether the hydrogen atoms are positioned in a regular pattern around the oxygen atom, if the hydrogen atoms are positioned in a random fashion around the oxygen atoms then the structure is proton-disordered. The main problem with proton ordering is that it doesn't always occur in a natural environment, even at low temperatures. This is because as the temperature falls, the movement of the defects in the hydrogen atom arrangement becomes slower, which is an issue as defects are necessary because they are what allow the hydrogens to rotate around the oxygen in the first place and so now that the defects are unable to move as much the hydrogen atoms are unable to correct their order.[2]

3.5) The Different Polymorphs of Ice

Fig. 8



Ice can take many different forms in a natural environment so how does water choose which polymorph to take? The answer is through the phase factors as pressure and temperature determine which structure is most favourable for the environment and so whilst there is only one form of gaseous and liquid water there are 16 possible ice polymorphs* for water to take and so this allows water some manoeuvrability under certain conditions. Pressure is a major factor for choosing a polymorph because; as the pressure increases more pressure is applied to the bonds in the structure which causes the bonds to be pushed out of their correct orientation which weakens the structure, whilst increasing the temperature causes the molecules to have more energy and makes it easier for bonds to be broken and so as the temperature increases it becomes harder and harder to keep the water in its solid state. There is another factor which is the rate of cooling water to form ice which can affect the amorphous structure that the ice has, although any amorphous phase of ice requires a very specific environment to form and so is incredibly unlikely to form in a natural environment. [2]

* This fact is commonly debated because there are some artificial polymorphs that can only be made in a lab.

3.6.1) Isotopes of water

An isotope is an atom that has a different number of neutrons but the same number of protons and electrons hence it is heavier/lighter but still has the same chemical properties that it normally has. Hydrogen has two stable isotopes: ^{1}H and ^{2}H (^{2}H is also known as deuterium or D). Meanwhile oxygen has three stable isotopes: ^{16}O, ^{17}O and ^{18}O. This means there are nine possible water isotopes because water contains two hydrogen atoms and so it is possible to have a water molecule with two different hydrogen isotopes (eg. $^{1}H^{2}H^{16}O$) but the most common isotope of water is $^{1}H_2{}^{16}O$. Heavier isotopes have a higher boiling point and melting point than lighter isotopes and so; on earth a lower concentration of heavy isotopes of water are found in the polar ice caps compared with the sea because heavier isotopes can condense at warmer temperatures and so fall into the sea as rain whilst the lighter isotopes remain in the clouds as a vapour, clouds which eventually will coalesce at the poles which are cold enough to cause the water vapour to condense or even undergo deposition.[6]

3.6.2) Mass Spectrometry

Mass spectrometry is an analytical way of measuring the molar mass of atoms and molecules through the use of a mass spectrometer. How a mass spectrometer works is through the following steps:

1. Vaporisation – The substance must be gaseous for the rest of the steps to work; this is easily achieved through gently heating the substance before releasing it into the vacuum maintained inside the mass spectrometer.

2. Ionisation – At least one electron is knocked out of orbit around the substance causing it to become positively charged.

3. Acceleration – The ions are attracted to a negative charge which causes them to all accelerate until they all have the same kinetic energy.

4. Deflection – The ions are deflected by a magnetic field according to their masses, the lighter they are the more they are deflected because their kinetic energy relies on their mass multiplied by their velocity so if they have a smaller mass then they will have a faster velocity as they all have the same kinetic energy.

5. Detection – The ions reach the negatively charged detector at which they all gain an electron to correct their number of electrons, which causes an electrical current to occur alerting the mass spectrometer to the arrival of the substance. The mass spectrometer then waits until all of the substance has been accounted for at which point it takes the results and draws up a mass spectrum.[7]

4) Discussion

In this section I am going to describe what type of environment the Shackleton crater provides and how this will affect the water molecules that may be found inside, I do feel inclined to mention however that water hasn't actually been found in the crater yet but high levels of hydrogen have been detected in that area and so it is more than plausible that water will be found in the crater.

4.1.1) What type of environment does Shackleton crater have?

The environment of the Shackleton crater is an unusual one as the crater has a rather restricted exposure to its surroundings which causes some unusual properties; for instance, the crater is constantly at such an angle to the sun that only the rim of the crater is regularly lit up and the bottom of the crater hasn't been exposed to major quantities of light in billions of years which in turn has caused the crater's internal temperature to drop to around 90 K (-183 °C). The moon itself has a mass of about 7.35×10^{22} Kg which is only 1.2 % of earth's mass and is not nearly large enough to create a strong enough gravity field to maintain an atmosphere and so the moon's surface is effectively in a vacuum environment.

4.1.2) Why will water be in the Shackleton crater?

Although no water has actually been found in Shackleton crater yet, many believe that water does exist in Shackleton crater because it manages to provide a natural environment for the process of cryocondensation to be carried out. This would occur through the following steps:

1. Water enters the crater as a gas – this will either be via random diffusion of particles that happen to enter the crater from above or the gaseous water will come up from the lunar mantle because of magmatic degassing during lunar volcanic eruptions (water crystals have been found in lunar mantle samples).[8]

2. The cold environment lowers the gaseous molecule's kinetic energy and the moon's gravity pulls the gas particles to the bottom of the crater.

3. Due to the cold surface of the crater's interior and the fact that the moon's surface is effectively in a vacuum cryocondensation can occur.[3] It is also worth noting that Shackleton crater would allow for cryocondensation to be carried out extremely quickly because the excessively cold crater would cause the gas particles to deviate far from the ideal gas law by shortening the intermolecular distances and so the molecules will be attempting to change their phase anyway.

4.2.1) What structure will water molecules have on the moon?

On the moon there is no atmosphere and the temperature tends to be rather low and so the favourable phase for the water molecules to take can only be gaseous or solid and so any water found in Shackleton crater will be part of a crystal lattice due to the incredibly low temperature however, what type of crystal lattice will form under those conditions as there are 16 different polymorphs for water to choose from. To find the answer to this question all you need to remember is the low pressure and low temperature that Shackleton crater provides and you'll quickly realise that the ice will be in the ice I group (excluding the LDA, HAD and VHDA polymorphs which do fit into the ice I group but they require high pressures to form which can't be found on the moon's surface).[2]

4.2.2) Cubic ice

Fig. 9

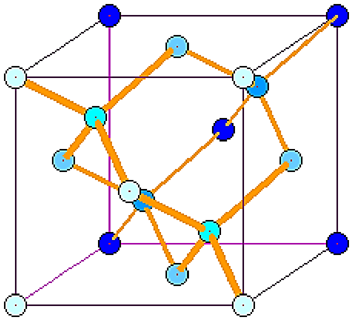
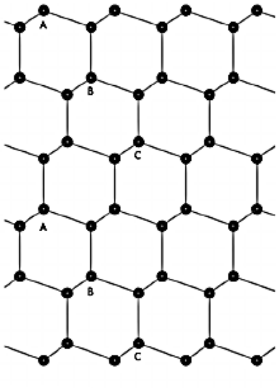


Fig. 10



(b) Cubic ice

Cubic ice fits into the ice I group and uses a cubic close packing arrangement of water molecules, which actually has an identical arrangement of oxygen atoms to the carbon atoms in the structure of a diamond. It is called cubic ice as it is composed of cubic unit cells and it is commonly referred to as ice Ic. Cubic ice can be found in the earth's upper atmosphere but it requires such a low temperature to form that it can't be found in a natural environment on the earth's surface however, Shackleton crater provides an ideal environment for its formation. Cubic ice is a relatively weak polymorph of ice and is commonly referred to as *metastable*, which means that the cubic ice structure is not actually the stable structure ice should naturally form but is instead a mildly stable, long-lived structure that will eventually transform into the stable structure. This occurs when the structure is warmed over -80 °C, at which point the cubic ice reforms into hexagonal ice.[9]

4.2.3) Hexagonal Ice

Fig. 11

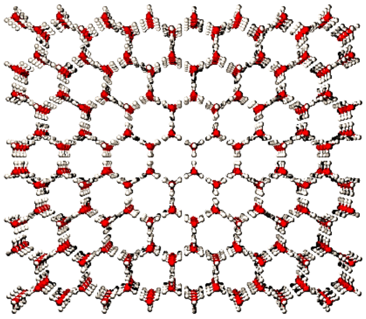
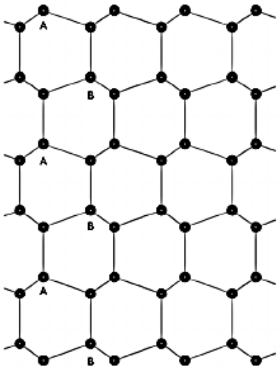


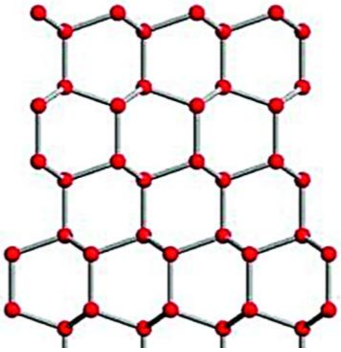
Fig. 12



(a) Hexagonal ice

Hexagonal ice consists of interpenetrating lattices, which have a hexagonal close packing stacking arrangement; it is commonly called ice I_h. This form of ice is much more stable than cubic ice and so can form at warmer temperatures of 273 K, which makes it the predominant form of ice found on earth. Hexagonal ice can form at the same temperatures as cubic ice and also; whilst cubic ice can be reformed into hexagonal ice, the situation can't be reversed.[10] The proton-ordered form of hexagonal ice is called ice XI and it is an extremely stable structure but, it can only be formed below 72 K and so it will almost certainly not be found in Shackleton crater.[12]

Fig. 13



4.2.4) Stacking Disordered Ice

Stacking disordered ice, or ice I_{sd}, is a form of ice which uses alternating sheets of cubic ice and hexagonal ice, it is surprisingly common due to the fact that hexagonal ice can form at the same temperature as cubic ice not to mention it is actually a more stable structure than cubic ice even though it too is *metastable*.[11]

4.3) Why is finding water isotopes on the moon important?

The Lunar Mission One probe will be fitted with a small mass spectrometer so that it can analyse some of the samples it collects on the moon, this type of analysis will also allow the probe to identify isotopes found in a sample which could be incredibly useful when examining water. The reason that finding water isotopes is important is because these isotopes could be evidence for some major scientific theories which have yet to be proven. For instance, the water found on the moon so far have an unusually high deuterium to hydrogen ratio which actually supports the theory that water isotopes could provide evidence for the giant-impact hypothesis.[8] This hypothesis states that billions of years ago a gigantic celestial object (believed to be about the size of mars) collided with the earth and the moon was formed from the rubble of this collision. If this did occur than an enormous amount of heat energy would have been produced, enough to vaporise entire oceans. The gaseous water molecules produced would have been drawn towards both the earth and the debris of the celestial object as they both have a large mass, until when the gas particles reached an equilibrium through diffusion. Then when the debris coalesced to form the moon; some water particles would have been trapped inside the newly formed lunar mantle. So originally, the water would have had a similar water isotope ratio to that of earth's but over time, as more meteors fell to earth with water, the ratio of water isotopes would have been altered drastically. This water would be originally found inside the lunar mantle but as mentioned previously, some of the ice that might be found in the Shackleton crater could have originated from magmatic degassing during lunar volcanic eruptions; whilst the rest would have been delivered to the surface by a meteor in which case, the ice would undergo sublimation and could then diffuse into the Shackleton crater. The reason that this water could provide evidence for the giant-impact hypothesis, despite being so different from earth's water, is because the only other possible way water would arrive on the moon is through a common origin for the water in our solar system, but if this were the case then the water isotope ratio would be much more similar to earth's.[8]

4.4) Conclusion

When Lunar Mission ne is collecting water samples from the Shackleton crater, I would suggest that they avoid contaminating the water samples, like many of the Apollo missions did, by placing the ice into a container made of a hydrophobic material so that the water will be unaltered before it is examined. These containers would then have to be kept below -80 °C to prevent any cubic ice structures from converting to hexagonal ice. I would also suggest that the ice is placed into these containers before it is removed from the Shackleton crater as once the ice is heated enough by the sunlight it will undergo sublimation and vaporise.

As for the future manned base possibility and the option of using any ice found in the Shackleton crater as a resource, I would remind the project that the water will be unable to become a liquid and so the water will have to be cut out of the ice on a regular basis, transported to the base, melted and filtered before it would be safe to use and so; whilst it is possible to use the ice as a resource it will not be an easy task for the astronauts to carry out.

5) Evaluation

I believe that my research techniques were a little scattered because it was quite inconsistent, this was mainly due to the fact that I found it hard to get my hands on relevant research papers to read through and when I could much of the information I found incomprehensible. However, over time, I learnt how to search for information that was relevant and I made sure to keep detailed notes throughout to make it easier to grasp. Occasionally I was unable to find relevant papers and so resorted to using multiple websites which contained the information I was looking for and when we were later shown how to access research papers I double checked that the information was accurate. So overall I would say that my research technique is fairly reliable although perhaps not the quickest way of going about it.

6) References

1. Averill, Bruce & Eldredge, Patricia. (2006). General Chemistry: Principles, Patterns and Applications (1st edition). Prentice Hall.

2. Dutch, Steven. (1998). Ice Structure. Available at: https://www.uwgb.edu/dutchs/Petrology/Ice%20Structure.HTM. Accessed: 06/08/2016.

3. Day, Chris. (2006). Basics and applications of cryopumps. Available at: http://cds.cern.ch/record/1047069/files/p241.pdf. Accessed at: 03/08/2016.

4. http://www.thebigger.com/chemistry/surface-chemistry/distinguish-between-physical-adsorption-and-chemisorption/. Accessed at: 04/08/2016.

5. Lower, Stephen. (2003). A gentle introduction to water and its structure. Available at: http://www.chem1.com/acad/sci/aboutwater.html.

6. West, J.B. *et al*. (2010) Isoscapes: Understanding Movement, Pattern and Process on Earth through Isotope Mapping (1st edition). Springer Science + Business Media.

7. Clark, Jim. (2000). Available at: http://www.chemguide.co.uk/analysis/masspec/howitworks.html. Accessed: 14/08/2016.

8. Greenwood, James *et al*. (2011). Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon (1st edition). Published online.

Chaplin, Martin. (2000). Water Structure and science. Available at:
9. http://www1.lsbu.ac.uk/water/cubic_ice.html. Accessed at: 08/08/2016.
10. http://www1.lsbu.ac.uk/water/hexagonal_ice.html. Accessed at: 08/08/2016.
11. http://www1.lsbu.ac.uk/water/ice1h1c.html. Accessed at: 08/08/2016.

12. Raza, Zamaan *et al*. (2011). Proton ordering in cubic ice and hexagonal ice; a potential new ice phase – XIc (1st edition). Published on http://pubs.rsc.org | doi:10.1039/C1CP22506E.

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