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# MASTER THESIS

## Assessment of oxygen production on the Moon through reduction of Ilmenite

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**Universitat Politècnica de Catalunya**  
**Master in Aerospace Science & Technology**  
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# **Assessment of oxygen production on the Moon through reduction of Ilmenite**

BY

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Submitted in partial fulfillment of the requirements of the  
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## ABSTRACT

*In the past 20 years, considerable attention has been paid to returning to our natural satellite with robotic and, eventually, manned mission(s) not only to continue one of the most scientifically fruitful exploration programs in history, but also to open new perspectives on engineering in planetary surfaces through lunar resource utilization. Among the so-called lunar resources, oxygen is probably one of the most needed and versatile. Applications of this gas range from fuel to life-support systems. However, oxygen in the Moon is present not as an atmospheric gas but combined with other elements forming minerals. Despite its very large abundance (almost 50% of the mineral material may be oxygen) its extraction and exploitation requires some technologies of not-so-straightforward application in a hostile environment such as the lunar surface. Among these technologies, hydrogen reduction of ilmenite ( $\text{FeTiO}_3$ ) has shown to be one of the most promising. This mineral is abundant in the high-Ti basalts, identified in the Apollo XI and XVII landing sites. Processing of ilmenite with molecular hydrogen at temperatures of about  $800^\circ\text{C}$  yields to the formation of metallic iron, titania ( $\text{TiO}_2$ ) and water. This latter product, can be electrolyzed with relative ease to produce oxygen and hydrogen which, in turn, can be recycled back to the initial reduction process. Recent evidence of lunar water may add new hopes to considering the potential utilization of the ilmenite reduction process for oxygen extraction. Our work aims at providing additional information on the hydrogen and water estimations on the moon and on the mechanisms and kinetics of ilmenite reduction in order to optimize the operation of an eventual ilmenite processing unit (IPU) on the lunar surface. A variety of terrestrial ilmenites close in composition to the lunar samples have been characterized and treated with a Temperature-Programmed-Reduction (TPR) procedure. TPR allows a quantitative evaluation on the effect of temperature on the amount of hydrogen "absorbed" by a system, as well as the products and ultimately the efficiency of such reaction. In this paper, such parameters have been studied at temperatures between  $100$  and  $900^\circ\text{C}$ , at different scan rates in order to assess the efficiency of the utilization of hydrogen on the lunar surface. Scanning rates very high affects the equilibrium of the conversion, and very low ones change the expected behavior of the curve during the reduction and it can cause instabilities. A good value of scanning rate has been determined around  $10^\circ\text{C}/\text{min}$ .*

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*...to those who worked hard from their desks,  
behind the cameras, to bring humans to the moon.*

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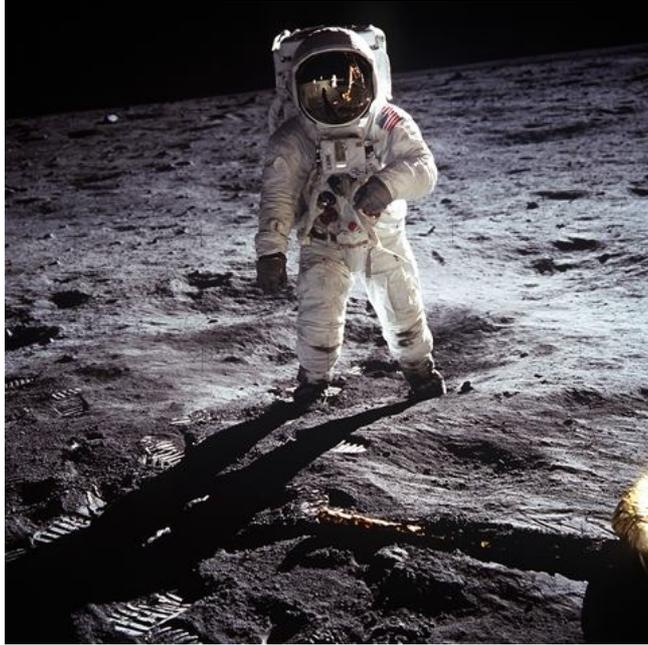
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# 1. PROJECT STATEMENT

This master thesis evaluates the existing in situ resource utilization technologies and human needs to go to the moon. Its mission statement is:

To evaluate the natural resources of the moon related with the human needs and to asses a process to obtain Oxygen from the regolith of the moon determining its feasibility by using thermo gravimetric techniques.



**40<sup>th</sup> Anniversary Apollo 11.** Astronaut E. Aldrin during the first walk on the Moon, in 1969.

*'The moon is the first milestone on the road to the stars'* \_ **Sir. Arthur C. Clarke**

*'Earth is the shore of the Cosmic Ocean'* \_ **Carl Sagan**

*'The man with a new idea is a crank until the idea succeeds'* \_ **Mark Twain**

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## 2. INTRODUCTION

The Moon has always been one of the main targets since the beginning of the space career. Apart of being our closest planetary neighbor and all the opportunities that this opens, a renewed interest in lunar exploration has already translated on exploration technology missions such as Lunar Prospector (1998 NASA), SMART-1 (2003 ESA), Selene (2007 JAXA) and Chandrayaan (2008 ISRO) and the recent Lunar Reconnaissance Orbiter (2009, NASA) and Change-1 (2007, CNSA). In the past 20 years, considerable attention has been paid to returning to our natural satellite with robotic and, eventually, manned missions to continue one the most scientifically fruitful exploration programs in history but also to open new perspectives on engineering in planetary surfaces through lunar resource utilization.

Among the so-called lunar resources, oxygen is probably one of the most needed and versatile. Applications of this gas range from fuel to life-support systems. However, oxygen in the Moon is present not as an atmospheric gas but combined with other elements forming minerals. Despite its very large abundance (almost 50% of the mineral material may be oxygen) its exploitation requires some technologies of not-so-straightforward application in a hostile environment such as the lunar surface. Among these technologies, reduction of ilmenite ( $\text{FeTiO}_3$ ) with hydrogen has shown to be one of the most feasible and promising.

This mineral is abundant in the high-Ti mare basalts, identified in the Apollo XI and XVII landing sites. Processing of ilmenite with molecular hydrogen at temperatures of about  $800^\circ\text{C}$  yields to the formation of metallic iron, titania ( $\text{TiO}_2$ ) and water. This latter product can be relative easily electrolyzed to produce oxygen and hydrogen. The work to be carried out aims at providing additional information on the mechanisms and kinetics of ilmenite reduction in order to optimize the operation of an eventual ilmenite processing unit (IPU) on the lunar surface. A variety of terrestrial ilmenites close in composition to the lunar samples will be characterized and treated with a Temperature-Programmed-Reduction (TPR) procedure. TPR allows a quantitative evaluation on how temperature affects the amount of hydrogen "absorbed" by a system, as well as the products of such reaction.

### 2.1. In situ Resource Utilization

#### 2.1.1 Human Space Career and the human involvement evolution.

The exploration of space, during its more than fifty years of history, has been creating a necessity of improvement in most fields of science and technology.

During the first years since the beginning of this space exploration, the main objectives were the study of the Earth and in general, the Universe with the help of satellites and telescopes; that is essentially, unmanned missions. The space has been considered a hostile place for humans but privilege environment from the scientific point of view. Many missions are still using robotic science to achieve the objectives avoiding the life support part of the mission. However, it is known that the human is the most precise and powerful robot we have but most fragile [Cockell,

2005]. During the last years, the manned missions have increased since the first astronaut went to the Space, Yury Gagarin in 1957, since today with space laboratories working on. The past MIR and now the ISS are an example of this new kind of space exploration. Different astronauts are living there for short periods of time while they are doing different experiments and research on board. For these short periods of time, the needs of an astronaut can be supplied with Earth source elements that they bring with themselves in the missions or with some special re-supply missions, such as the ATV (Automated Transfer Vehicle) Jules Verne (ESA, 2008).

However, the future is going in a different direction. The Human Exploration of Space is now pointed to go back to the moon and to start developing technology to put a man on Mars, as we did with the moon in the last century. President Obama was very clear on the year 2010 budget of the USA: 'The NASA will return humans to the moon while also supporting a vigorous program of robotic exploration of the solar system and universe'. *Constellation Program* was born to satisfy this new vision of Human Exploration on returning back to the moon and going beyond and to be able to study and learn how to live there. Ares launch vehicle, Orion crew capsule and Altair Lunar Lander are some of the space capabilities that are being developed by NASA. This new challenge (which can be summarized in: '*To the Moon, Mars and Beyond*' SSP09) requires not only an advance in technology but a different and most difficult preparation in specific fields such as propulsion, life support systems, psychology adaptation, communications... especially in the human aspect. [NASA Web Page, 2010 and USA Space Budget, 2010].

The greatest way to go to Mars and the one taken into consideration for human exploration is to set up a lunar base with two main objectives: as a launch facility to stop in the way to Mars, it decreases the propellant weight and cost and can provide supplies; and to launch missions such as the ones with near-earth objects as targets; and as a permanent laboratory. This will mean not ever short-term missions with just a small crew lander; the first wall to break is to learn how to live in that hostile and not-atmosphere environment. The easiest way to cover the human necessities on these long-term missions, apparently or at least in terms of profitability in short time, is the Earth re-supply. It means bringing from Earth all the needs for the astronauts in the Space, but this is not profitable and feasible for long-term missions, because the cost to put in orbit any object from Earth will be higher than the benefits obtained of living in Space. The solution then, is the In-Situ Resource Utilization (ISRU).

### **2.1.2. The ISRU related to Human necessities**

The ISRU works to establish, evaluate and assess the in situ resources available on the planets or mission scenarios and the technologies needed to utilize and exploit these resources [NASA web Page]. All the Space Agencies over the world work to improve this technology. There are currently many projects on board, working to obtain feasible methods with the main objective of decreasing the costs in not only Low-Earth Orbit missions, but looking beyond: for the future deep space and near-earth objects missions.

The research and technology development areas of the ISRU will focus on technologies necessary to extract consumables (O<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, He, etc.) for human life-support system replenishment (ECLSS, EVA, etc.), source materials (feedstock)

for In Situ Fabrication and Repair (ISFR) technologies, and source materials (composites, etc.) for radiation shielding and shelters from in situ resources (lunar or Martian regolith and atmosphere), see figure 2.1. The transformation of in situ space resources into useful materials is being studied through fundamental and applied experimental research, theoretical modeling of processes, and technology development on the areas like extraction, purification, transformation, shaping or characterization processes [NASA Web Page, 2].

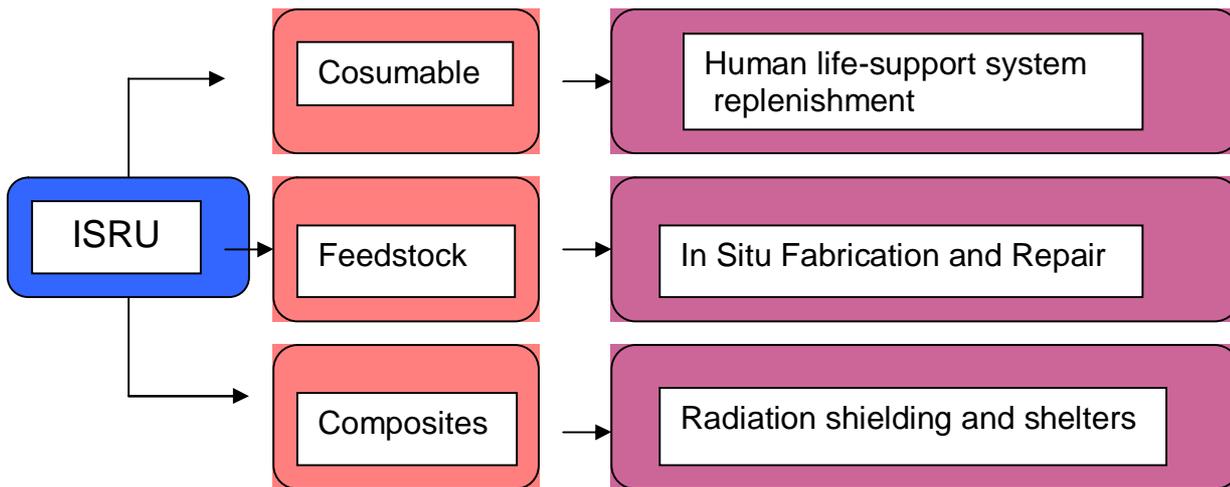


Figure 2.1. Scheme of the ISRU study.

In conclusion, the major target of the ISRU is to cover the main human necessities to set an extraterrestrial base to live beyond the Earth. The next step is to start using these in-situ resources to develop themselves in that hostile and non-terrestrial environment: get construction materials, storage and reuse energy..., with a final objective: to be self-sufficient in space.

However we should bear in mind that needs to survive are as important as the wastes in long-term missions. Part of them should be recovered and recycled to maintain a correct vital cycle and avoid contaminants. Planetary protection policy done by (Committee on Space Research) COSPAR in 2005 is very strict at this point [COSPAR, 2005]. So recycling is one of the most important issues, not only on Earth but on Space. In the next figure it is possible to see a summary of the main human necessities and wastes per crew member per day.

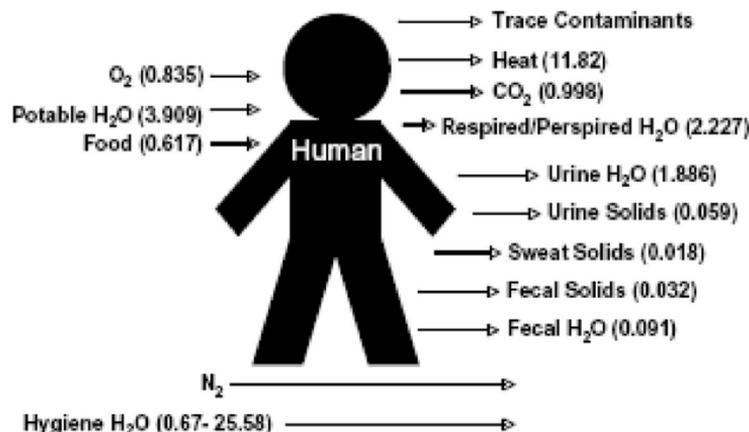


Fig 2.2. Human Consumable and throughput Values in kg/crewmember/day

The next table shows in more detailed way the necessities and wastes in kg that a human consumes in one day.

As shown in figure 2.2 astronauts consume a mean value of 0.98 kg of O<sub>2</sub> per day, producing 0.8l of CO<sub>2</sub> for every liter of O<sub>2</sub> they breathe. For example, during the Apollo missions, the average water consumption per astronaut was 0.85 kg per day. However, astronauts need an average of 1.6 kg of water to sustain each of them every day, sometimes it could be higher (around 2.2 or 2.5l per day) and until 27 additional kilograms for other purposes (hygiene, food...). However, life support systems are more complex than initially imagined and should cover more needs and not just the lack of oxygen, water and food.

According to NASA, to put even one of these kilograms onto orbit costs \$25,000 [Grossman A., Armstrong M. et al.].

### 2.1.3 Example of a long-term mission: Lunar Base

Oxygen is the essential element for a manned mission; humans can only survive some minutes without oxygen. The first question to answer when analyzing the oxygen production methods is:

- will be those methods able to cover at least the elemental needs of a human in space assuring at the same time that the effort and energy used will compensate the amount of O<sub>2</sub> obtained?.

Answering this question is called 'feasibility analysis' and it is essential on the evaluation of new technologies and its future uses.

The first step of this analysis is to quantify, as precise as possible, the necessities of a human for each specific mission in order to establish the minimum requirements needed. There is an example of this study in the next table, which shows the total necessities of a crew living in a Lunar Base [Space Systems Engineering Project, MAST 08]. The study was based on a crew of 10 people living in a lunar laboratory during 180 days (be aware that the transfer stage is neglected).

| <b>Necessities</b>             | <b>Total amount for 180 days stay On Moon</b> |
|--------------------------------|---|
| O <sub>2</sub>                 | <b>734.4 kg</b>                               |
| Air for EVA airlock manoeuvres | <b>144.0 kg</b>                               |
| Water (total needs):           | <b>18 876.0 kg</b>                            |
| For hygienic purpose           | <b>16 560.0 kg</b>                            |
| Drinking water                 | <b>2 016.0 kg</b>                             |
| For EVA suits                  | <b>300.0 kg</b>                               |
| Foods                          | 1922.4 kg                                     |
| Unique items                   | 541.1 kg                                      |

|  |               |
|--|---------------|
| Human metabolic wastes                   |               |
| CO <sub>2</sub>                          | 892.8 kg      |
| Water vapour                             | 2124.0 kg     |
| Energy                                   | 10 396 800 kJ |
| Other human wastes                       |               |
| Solid (feces, packaging, towels, cloths) | 1 509.1 kg    |
| Liquid (urine, vomits, hygienic water)   | 17 209.6 kg   |

Table 2.1. Amounts of necessities in a lunar base for 180 days mission.

The figure 2.3 below shows a complete and more detailed scheme of a life support system for a 6 crew members base.

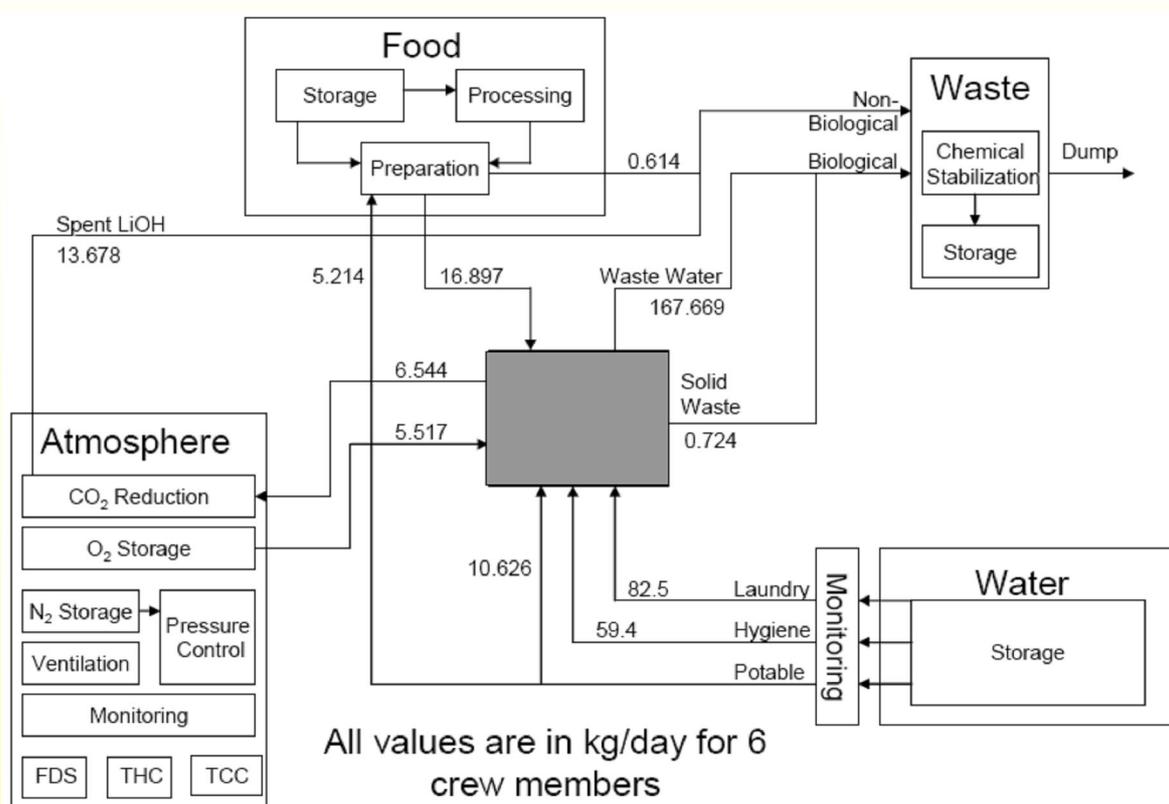


Figure 2.3. Scheme of a life support system for 6 crew members.

Summarizing and focusing on the oxygen required (in blue in table 2.1), for a crew of 10 member during a period of 180 days on the moon, it is necessary 878.4 kg of gas Oxygen and 18.876kg of water (which also contains oxygen).

### 2.1.4. Lunar Resources

The next step after the total oxygen amount needed is quantified is the evaluation of the existing processes to obtain this oxygen to determine if they accomplish the

minimum requirements. However, before being able to do that it is important to know which are the available lunar resources and in which quantities can be found.

In order to analyze different processes to obtain oxygen, it is important to specify which of the available lunar resources are used in those processes, as mentioned before. For instance, it is weird to propose a method in which the sodium is needed if there is not sodium on the surface of our mission scenario. In other words, the In-situ Resource Utilization needs to identify which are those resources in the mission scenario and specify the level of importance and which can be the future uses of those resources.

Focusing on the moon, Lunar Resources are mainly important for humans for two purposes: to supply fuel and to support life for planetary travel. The identified resources in the moon are oxygen, iron, titanium, aluminium, magnesium, silicon, silane (SiH<sub>4</sub>), Helium-3, Hydrogen and many others [Ness R.O., 1990].

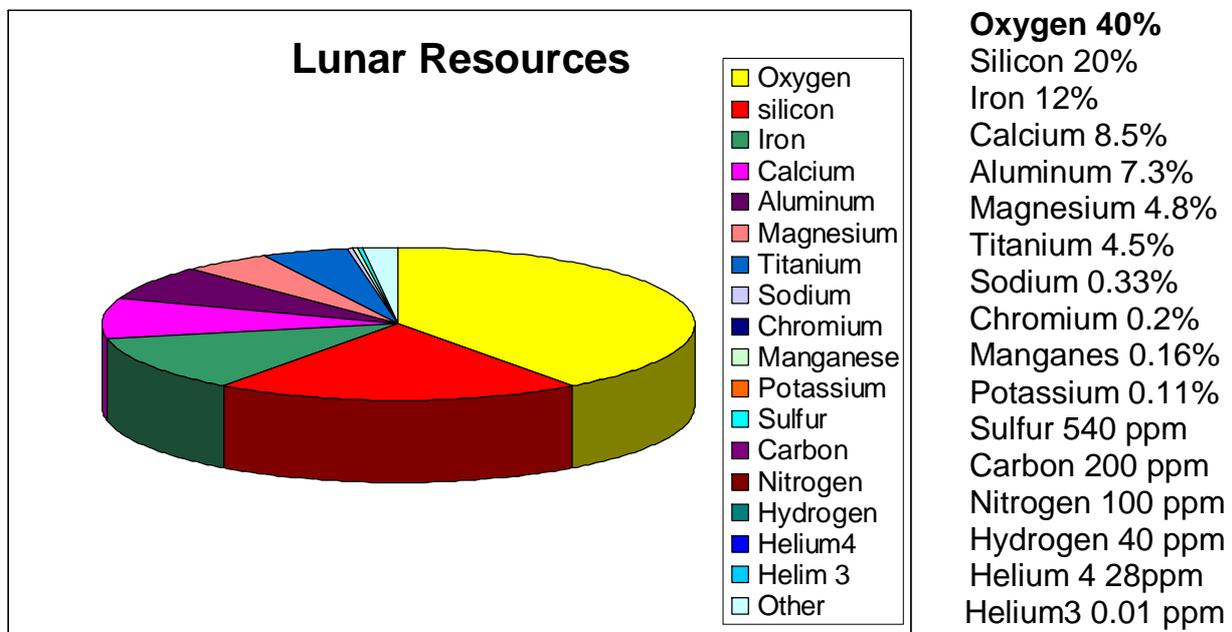


Figure 2.4 . Lunar Resources and its percentage of quantity.

Apart of those purposes there are two possible markets that make the Moon an attractive source of materials: launch base to objects beyond the LEO (Low Earth Orbit) and as a replacement for some terrestrial materials when they start to exhaust. One interesting factor that the Moon can offer in comparison to the Earth is that due to the low gravity in the moon is easier to transport a given mass from the lunar surface than from Earth (lower escape velocity in the moon), remember that NASA estimate the cost of boosting into orbit a kilogram of oxygen in \$25,000. This is crucial for future missions to Mars with a stopover in a moon base. Rocket propellants tanks have to be filled up from the Earth for missions to deep space and most of this mass is to bring it just to low-Earth orbit. That means that having the possibility of filling directly with propellant from the moon will decrease considerably the cost of such deep space missions.

Another important market is the possibility of using lunar materials on Earth due to the probable future scarcity of some terrestrial elements, or just because they are not available on Earth. One example could be the isotope He-3, which is collected on the lunar regolith due to the Solar Wind exposure (0.01ppm is He-3 and 28ppm is He-4 in the regolith). This kind of isotope is useful for nuclear fusion, instead of using the actual tritium. [Heiken, G.H at al, 1993 and Slyuta, E.N., at al, 2007].

This project is focused on the exploitation of one of these elements found on the moon, the element that form 60% of the total weight composition, which is the oxygen, by using also some of the elements listed above as lunar resources.

## 2.2. Lunar Oxygen

As explained in the previous section the Oxygen is the most, or one of the most important elements needed for the humans to live in the absence of atmosphere, but it is not only important and useful for life but also for propulsion systems as a propellant and oxidizer.

### 2.2.1 Importance of the oxygen: Main uses.

There are two major uses proposed for lunar O<sub>2</sub>:

- In propulsion systems
- Life support purposes.

Many existing rockets use this element as oxidizer in the propellants. Liquid O<sub>2</sub>-Liquid H<sub>2</sub> rockets are considered most likely, because most of the mass is propellant which means Oxygen. Some examples of rockets that use this kind of propellants (LH<sub>2</sub>/LOX) are: the main engines of Space Shuttle, Ariane 5 (figure 2.5) main stage and Ariane 5 ECA second Stage, the first stage of Delta IV, the upper stages of Saturn V, Saturn IB and Saturn I and Cenatur rocket. These ones are used in last important missions, like Apollo's and are still used by the main Space Agencies, because its advantages: lightweight, density similar to water, good mixture ratio... (Sherwood and Woodcock, 1993).

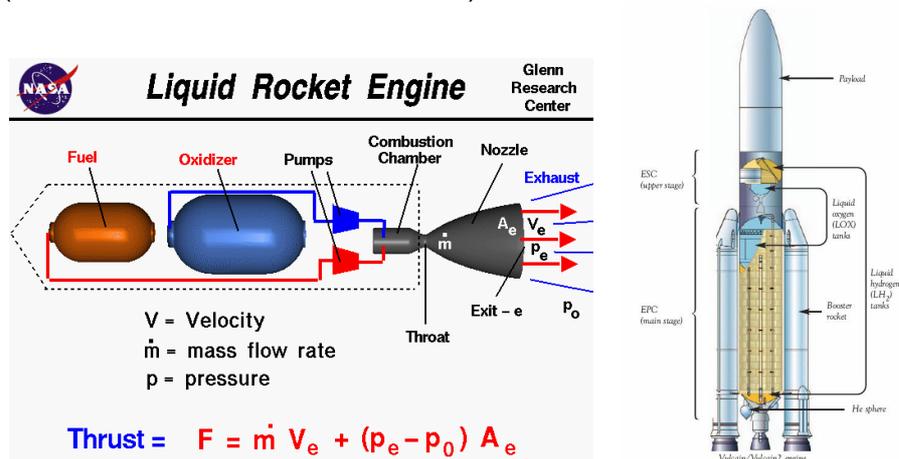


Figure 2.5. Liquid Rocket Engine and Ariane 5. [NASA web page and www.fluent.com]

The second major use is using oxygen as an essential element for life support functions. The human presence in the moon is on the next objectives of the Space Career so the necessity of having oxygen in gas state without the necessity of a periodic transportation from Earth is essential.

The production of lunar liquid oxygen could result in huge cost savings on propellant for transport systems and in the avoidance of the high costs of bringing the oxygen from the Earth.

### **2.2.2. Main Constraints with Lunar oxygen.**

It may seem contradictory for a planet without atmosphere, but the most abundant element in the moon is the Oxygen. More than 60% of the atoms are oxygen, but all of them are bound up chemically to other elements in the regolith and rocks and as an adsorbed gas originated by the solar wind [Sherwood and Woodcock, 1993 and Heiken et al., 1991]. Oxygen is not only in atom-percent the most abundant but also in weight-per cent which is around 45% of the total (see figures in ISRU section). Oxygen is considered what is called one of the '*Major Elements*' in the moon.

The first requirement then is accomplished: there is oxygen in the moon. Bearing in mind again the needs of a human it is necessary to specify that the required oxygen for humans must be at gas state for life support necessities or liquid, for propellant uses. This state of the element is almost nonexistent in the moon and its accessibility is a key problem. The solar wind implanted oxygen is low enough to force processing huge amounts of regolith to get it in large quantities, and oxygen is hard to extract directly from rock. Luckily, there have been studied several processes to obtain oxygen from minerals that contains it chemically bounded which seems to be quite reliable.

### **2.2.3. Processes to obtain Oxygen in the moon**

The production of oxygen in a gas form utilizing in-situ materials is very important for a human lunar establishment. More than twenty different processes to produce oxygen from lunar materials have been proposed along the whole Space Career. Most processes are extremely complicated and difficult to implement or just have been untested. Simplicity, energy requirements, nature of feedstock, quantity of lunar ore and resupply mass are the main factors when evaluate the feasibility of a process [26 Taylor, 1993].

Oxygen through photosynthesis [25 Hareland, 1988] is one of those proposed methods to obtain oxygen and the most known, especially because of its appearance in many science-fiction films. A biological Green House could help providing a continuous supply of oxygen required for the crew. The major problem is that the plants used to create this oxygen are very difficult to maintain because they follow a light cycle, in which during a period of time they are consuming oxygen. The objective is to maintain good values of the gas playing with the light [ACCESS MARS Project, 2009]. However, this method is not catalogued as ISRU one, because the main resource (plants) must be taken from earth and resupplied at some point.

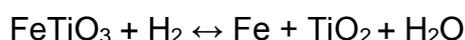
In following sections, in situ resource utilization methods are going to be briefly explained. There are different ways to get oxygen using lunar resources by many different processes in which different energies, elemental ores, reactants, or methods are used. [38 Taylor and Carrier].

### **2.2.3.1. Solid/Gas Interaction**

Lunar Ores can be reacted with gases in order to produce Oxygen.

#### Ilmenite Reduction with H<sub>2</sub>

Ilmenite makes up 10 to 20% by volume of some hi-titanium mare basalt rocks and in less quantity of mare soils. The kinetics of this reaction is faster than using silicate minerals and oxygen constitutes the 10.4 wt% of the products.



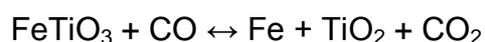
Reaction temperatures of 700 to 1000C are needed to obtain suitable reaction rates, the water produced is electrolyzed and the hydrogen is recycled.

Ilmenite reduction is one of the preferable because the energy required to reduce the FeO in Ilmenite to Fe+1/2O<sub>2</sub> is relatively low (increment of H for the reaction is about +9.7kcal/g-mol at 900°C).

This process will be more detailed explained in following sections.

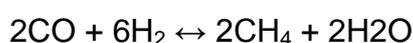
#### Ilmenite Reduction with C/CO

The carbon monoxide is used as a reductant. In this case the product is carbon dioxide instead of Hydrogen, which must be broken to liberate oxygen, this process will require significant energy, but it has been demonstrated that there is solar-wind implanted carbon in the soil (20-30ppm), and particularly in Ilmenite.



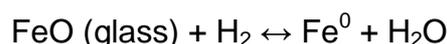
#### Ilmenite Reduction with Methane

This reduction by methane could take similar process as the one explained before. CO and 2H<sub>2</sub> are products that with additional H<sub>2</sub> at 800 to 1000C can produce water.



#### Glass Reduction with Hydrogen

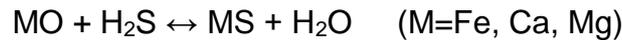
Lunar glass, especially from mare regions can contain FeO up to 20wt%, and it has been demonstrated that this glass can be easily reduced by hydrogen.



The main advantage of this process is that the glass is abundant in the lunar regolith (from volcanic activity and meteorite impacts), but the process has not been studied enough to determine its feasibility.

#### Reduction with H<sub>2</sub>S (hydrogen sulfide)

This is a process which seems theoretically simple but it becomes more difficult when applied. If the silicates are not easily broken, the kinetics is slow and complicated. Moreover the oxygen should be purified thoroughly due to the toxicity of the hydrogen sulfide.



#### Extraction with Fluorine

Despite that the fluorine gas is highly reactive and the reaction using anorthite occurs at the first stage, the danger of working with fluorine is a major safety consideration.

#### Carbochlorination

The positive point of this process is that can be done using bulk lunar soil, either mare or highlands, but the large number of steps during the reaction is a negative point, because add complexities and problems, so it is not going to be detailed.

#### Cl<sub>2</sub> Plasma Reduction

It is not possible to evaluate this process, it is still under evaluation and it has not been tested yet.

### **2.2.3.2. Silicate/Oxide Melt**

Soil with their minerals and bulk rock in a molten state can be acted upon to produce oxygen.

#### Molten Silicate Electrolysis

It is based on a process to immerse two electrodes in a vat of molten silicate liquid and imposing a current between the electrodes. The number of process steps and equipment is low and oxygen is liberated with no necessity of electrolysis.

#### Fluxed Silicate Electrolysis

The use of a flux to dissolve the silicate feedstock can smooth some difficulties of high-temperature corrosion. It also has lower energy requirements, and the oxygen is recovered directly from the anode.

#### Caustic Silicate Electrolysis

Molten NaOH at 400C is used to dissolve minerals from bulk lunar soil; the oxygen is yield by electrolysis at the anode and sodium at cathode.

#### Carbothermal Reduction

This process produces oxygen using molten reactant (such as ilmenite or anorthite) and involving carbon in some way.

It is a very complex process and it needs a large quantity of energy due to the high temperatures needed for the process.

### Magma Partial Oxidation

The first step is to extract FeO from the rock using a magnetic field which can separate it from the remainder of rock components. It is high temperature electrolysis (1300-1400°C) where molten magma is at the anode and the high iron material at the cathode.

### Li or Na Reduction of Ilmenite

It is a process which involves an indirect electrochemical reduction of lunar oxides using lithium or sodium to reduce oxides to metal and Li<sub>2</sub>O.

## **2.2.3.3. Pyrolysis**

Pyrolysis is the chemical change induced by the application of heat (usually a partial decomposition)

### Vapour phase reduction

High temperatures (2200-2700°C) during the vapour pyrolysis are used to vaporize the feedstock and transform oxygen-bearing compounds into monoxides and oxygen. After vaporization, the gas is immediately cooled and the oxygen is condensed.

### Ion Plasma Pyrolysis

At very high temperatures (7000-10000°C) oxide dissociation products are ionized. The highly ionized metals are extracted and the neutral oxygen (only 1% of this material is ionized) flows downstream to be collected.

### Plasma Reduction of Ilmenite

This is a more efficient way to extract oxygen from Ilmenite, but more energetic consumption: the temperatures proposed are between 3000°C and 6000°C, at which the elements are completely dissociated.

## **2.2.3.4. Aqueous Solutions**

### HF Acid Dissolution

The lunar regolith is dissolved to create metal fluorides and water. This is a complex process.

### H<sub>2</sub>SO<sub>4</sub> Acid Dissolution

This process planned a sulfuric acid dissolution process to digest an ilmenite feedstock.

## **2.2.3.5. Co.Product Recovery**

### H<sub>2</sub>-He-Water Production

With high temperatures (900°C) the lunar soil releases around the 80% of Hydrogen. This hot hydrogen can react with oxide materials to produce water.

## 2.2.4. Evaluation of the best process

Considering the evaluation done by L.A. Taylor and W.D. Carrier and taking into account the factors mentioned at the beginning of the section (technology readiness, number of steps, process conditions, feedstock requirements...), the eight processes considered the most feasible ones to produce oxygen in the moon are:

- Ilmenite Reduction by H<sub>2</sub>,
- Ilmenite Reduction by CO,
- Ilmenite Reduction by CH<sub>4</sub>,
- Glass Reduction with H<sub>2</sub>,
- Molten silicate Electrolysis,
- Fluxed Molten Silicate Electrolysis,
- Vapor Pyrolysis and
- Ion Plasma Pyrolysis.

Ilmenite and Hydrogen are key elements in many of these processes; both elements will be explained in more detail in following sections.

The Ilmenite reduction by H<sub>2</sub> is catalogued as one of the most feasible because this process passed with high punctuation all the analysis done, as follows:

Feedstock: There is a large quantity of Ilmenite in the moon, especially on the High-Titanium mares.

Technology: It is evaluated with an 8 over 10, (10 means no major unknowns or technologic developments). This means that most of the technology needed is known and already available.

Number of steps: 9 over 10 (10 is the minimum in the number of steps ranking). As the reaction has only 2 steps, the rest are the common ones: mining, beneficiation, etc... adding up very few number of steps.

Process conditions (temperature, energy, plant mass, corrosion): 7 over 10 (10 means low)

Another important factor is the quantity of hydrogen recovered after the process. It is known by previous studies that the product-to-reagent ratio minimum to be economically feasible is 50. With this value in mind, the recovery of hydrogen at the end of the reduction of ilmenite must be 84%.

| Processes                      | Product        | Reagent         | Required % Recovery of Reagent<br>Product /Reagent = Payback |     |           |      |      |
|--------------------------------|----------------|-----------------|--|-----|-----------|------|------|
|                                |                |                 | =10  | =20 | =50       | =100 | =200 |
| <b>Ilmenite: Hi-Ti Mare</b>    |                |                 |  |     |           |      |      |
| <i>Reduction with Hydrogen</i> | O <sub>2</sub> | H <sub>2</sub>  | 20   | 60  | <b>84</b> | 92   | 96   |
| Reduction with CO              | O <sub>2</sub> | CO              | 94   | 97  | 98.8      | 99.4 | 99.7 |
| Reduction with Methane         | O <sub>2</sub> | CH <sub>4</sub> | 91   | 96  | 98.2      | 99.1 | 99.6 |

Table 2.2. Reagent Makeup for Potential Oxygen Production Processes. [Taylor and Carrier].

The oxygen-obtained per ore-used is also very important, because a significant rate of 1000 tones/year (Table 2.3) of lunar oxygen will have a big impact in space transportation. The greater the throughput, the lower the actual percent recovery will be.

| Processes                      | Ore (T/year) |                      | Plant Mass (T) | Energy (MWyear) |
|--------------------------------|--------------|----------------------|----------------|-----------------|
|                                | Raw*         | Process throughput** |                |                 |
| <b>Ilmenite: Hi-Ti Mare</b>    |              |                      |                |                 |
| <i>Reduction with Hydrogen</i> | 210000       | 21000                | 200            | 3               |
| Reduction with CO              | 210000       | 21000                | 225            | 3.5             |
| Reduction with Methane         | 210000       | 21000                | 225            | 3.5             |

\* Assuming feedstock

\*\* Assuming aprox. 90% conversion of ilmenite

Table 2.3. Estimations about the need to produce 1000 tones of Oxygen per Year [Taylor and Carrier].

Raw (T/year) = 210.000 (assuming a feedstock of 50 wt% of ilmenite)

Process Throughput (T/year) = 21.000 (assuming 90% conversion of Ilmenite)

Plant mass (T) = 200

Energy (MWyear) = 3

## 2.2.5. Oxygen production: Cost and benefits.

Apart from the different issues from the chemical part (the reaction has not obtained a 100% punctuation), there are many other ones due to the production of oxygen such as from the technical or economical side [6 Sherwood and Woodcock, 1993].

### 2.2.5.1 Technical Side

#### Transportation Constraints

Propulsive vehicles consume and expel large amount of mass. Mass and volume constraints limits the size of the equipment that can be brought from the Earth, anything else requires to be assembled on the moon, for example one hundred tones are enough oxider for retanking a lunar lander four times, but the size of the lunar lander is the main constraint when design the transportation systems.

#### Environmental factors

The lunar surface is a difficult place to perform operations. Gravity is lower, it is 1/6 g, structures can be lighter, which apparently seems an advantage but the gravity is that much lower that weight cannot be used as on Earth for stabilizing bases and providing tractions. Radiation can affect the electronic systems, interfering on the control operations, and can degrade the physical equipments or materials. Vacuum is a direct consequence from the absence of atmosphere; this absence also means a large gradient in temperature between shadowed and lighted areas. It also

complicates the motor and electronics operations, basically because of lubrication (it evaporates easily in vacuum).

The lunar syndic cycle is 29.53 days, sunlight during two weeks and night during the next two weeks. During the night, the solar energy is not available, and difference between night and day temperatures are so extreme (110°C to -160°C).

The regolith dust is the worst environmental constraint: Almost half of the regolith particles are smaller than the human eye can dissolve and is very abrasive and sticky; it can also penetrate easily in the equipment: windows, lens, motors, electronics, etc. everything must be really well protected.

### Operations

The direct operation cost comes from the surface mining, production, and storage infrastructure. Storage of oxygen and liquid hydrogen is another constraint since use of liquid oxygen will tend the use of surface-based retanking facilities, which need extensive inspection, service and repair capabilities.

### **2.2.5.2. Evolutionary Side**

To support human habitation or any other ISRU activities there are many steps which are necessary to be conducted for long-term bases. Site work construction, excavating, filtering, separating and consolidating lunar regolith are the first problems to be solved. The next step is configuration of foundations, work areas, permanent roads or stabilizing landing pads and finally, everything involving any chemical product and then industrial products requiring manufacturing processes.

## **2.3 Lunar Hydrogen**

Hydrogen is one of the elements needed for lot of the previous chemical reaction methods. It is found very easily on Earth but more difficult on the moon. Over time, comets and meteorites continually bombard the Moon. Water-rich meteorites and comets, largely water ice, may leave significant traces of water on the lunar surface. Energy from sunlight splits the majority of the water into its constituent elements hydrogen and oxygen, both of which usually fly off into space immediately. Some water molecules, however, may have literally hopped along the surface and got trapped inside enormous craters, some 1240 km across and nearly 13 km deep, at the lunar poles. Due to the very slight inclination of the Moon's axis, only 1.6°, some of these deep craters never receive any light from the Sun, they are permanently shadowed. It is in these craters that scientists expect to find frozen water if it is there at all.

Although the Moon rock collected by Apollo astronauts from the equator area contained no traces of water, in 1994 Clementine mission suggested that small, frozen pockets of water ice (vestiges of water-ice comet impacts) may be embedded unmelted in the permanently shadowed regions of the lunar surface. Although the pockets are thought to be small, the overall amount of water was suggested to be quite significant, around one billion cubic meters. Four years later, in 1998, the

Lunar Prospector mission recognized the presence of water especially in the polar area and recent missions in 2009, the Chandrayaan and Lunar Reconnaissance Orbiter recognized the presence of OH molecules and water, and are still evaluating very valuable data from those missions. The presence of useable quantities of water on the Moon would be an important factor in terms of cost-effective, since transporting water (or hydrogen and oxygen) from Earth would be very expensive.

Hydrogen abundance in soils is typically around 50 to 100  $\mu\text{gH/gSoil}$  and even a cubic meter of mature lunar soil could contain up to 100-200gr of Hydrogen. Chandrayaan mission modeled that the abundance could be around 770ppm [Peters et al, 2009]. Deep Space Impact mission estimates the water content is around 0.3-0.5wt% [Sunshine et al, 2009]. You can see its distribution and major concentration in figure 2.6.

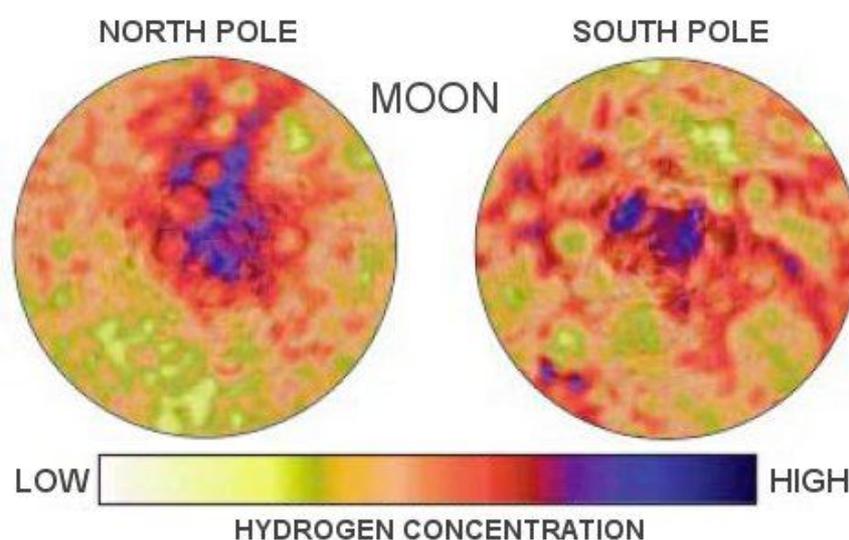


Image 2.6. Hydrogen concentration on the moon in blue, [NASA web page]

### 2.3.1. Origin of the Hydrogen in the moon

Hydrogen embedded in regolith grains has been found in returned samples, as well as has been detected by different missions, as mentioned before; the last ones finding evidence of this Hydrogen has been done by the Chandrayaan and LRO missions. Hydrogen on the surface of the moon is now undisputed data. This conclusion has been explained in terms of solar wind implantation, and provides one of several indicators of soil maturity; it has also been considered that Hydrogen has been delivered to the Moon in the form of water ice by comets and asteroids.(7 Feldman, 1998) In other words, the maturity of the soil influences directly the hydrogen content, because this kind of soil has been exposed to solar wind for a longer period of time, and the particle size in mature soils is finer due to the micrometeorite impacts, which increase the volume ratio particle and thereby the hydrogen ratio of the soil.

| Average Particle Diameter, $\mu\text{m}$ | Spheric % Vol. | % Hydrogen Content |
|--|----------------|--------------------|
| 10.0                                     | 1.195          | 51.34              |
| 32.5                                     | 0.369          | 17.11              |
| 60.0                                     | 0.200          | 9.73               |
| 82.5                                     | 0.145          | 6.38               |
| 120.0                                    | 0.100          | 5.03               |
| 200.0                                    | 0.060          | 4.36               |
| 375.0                                    | 0.032          | 4.03               |
| 750.0                                    | 0.016          | 3.01               |
| Total                                    | 2.117          | 99.99              |

Table 2.4. The relation between the particle size and the Hydrogen content is inversely proportional. Calculated for Apollo regolith fine sample 15021.

However, it is known that all the hydrogen found in the lunar samples from Apollo is not completely from the moon. About the half the H in early analysis of lunar soils is from terrestrial water contamination, because the samples were put when collection in Teflon bags that allow the pass of gases trough diffusion. The H concentrations in mature soils then, were about 50-100micrograms/gram as mentioned before. Usually the Hydrogen is compared with the amount of Helium found, many times the H/He ratio is used to express the quantity of H on the lunar soil. This is because the ilmenite retains He better than other minerals; the usual H/He ratio is around 2.

### 2.3.1.1. Solar Wind implanted element

The surface of the moon is not protected by any atmosphere; it is constantly exposed to the solar wind, which carries both hydrogen and helium, which are potentially very valuable resources. Actually, hydrogen is a major constituent of solar wind, and it is implanted in small amount in the lunar surface regolith [Heiken at al, 1991]. One natural variant of helium, helium3, is the ideal material to fuel fusion reactions. When scientists develop a better full understanding of fusion, and can practically implement these reactions, the Moon will be a priceless resource, since it is the best source of Helium3 anywhere in the Solar System.

The Hydrogen is abundant (20-100ppm) in various lunar soils and is easily recovered by heating the ilmenite from 600°C. The main reason, as said before, is that Ilmenite easily retains H and He.

The ions are embedded in the regolith particles to a depth of at least 100 to 200 nm and become trapped, but nearly the 85% of the H<sub>2</sub> is evolved during heating up to 700°C.

### 2.3.1.2. Comet and Asteroid deliveration element

Another part of the Hydrogen has been implanted on the regolith due to the impact of comets and asteroids. The majority of the hydrogen is implanted due to the process called spallation. In planetary science, spallation is known as the impact of micrometeorites in the surface of a planet or space abject.

Most of the materials are volatile due to the impact, because H is removed at high temperatures such as 700°C or more, but it is possible that part of this kind of implantation remains in constant shadow craters. If the amount delivered in any one impact is sufficiently small so that a thick atmosphere does not form, then a fraction of about 1/5 will migrate to both poles through an exospheric transport process.

However, it is thought that there could be higher amount of water just for assimilation of water of the regolith, this amount is quantified around 30 micromoles of water per gram of soil [Hodges, 1991].

The process in which water molecules get trapped into the regolith is because these molecules encounter spots that are sufficiently cold (mainly in permanently shaded craters near both poles), and when this happens they cover the surface where they can remain stably trapped for large period of time if the rate of loss does not overwhelm the rate of deposition. However, many comets are sufficiently large that a thick atmosphere should form due to the collision. The migration of water molecules to the poles has not been modelled, so the efficiency of deposition and the structure of the resultant deposits are not known. However it is thought that this cannot occur at mid-latitudes because impacts are inefficient to implant H at those latitudes where the energy released during the impact vaporizes volatiles. The water molecules are dissociated by solar UV (except for those migrating rapidly to cold areas) and escape the Moon's gravity field [17 Ness, 1992 and 12 Hall Cutler, 1992].

It is estimated that about  $10^{13}$  kg of water ( $0.5\text{kg/m}^2$ ) has been delivered to the lunar surface by comets over the past 2billion years (Clark, 2009).

### **2.3.2. Distribution of Hydrogen at the surface of the moon**

Several missions have detected hydrogen on the surface of the moon using different technologies, the most utilized one, used during more than 12 years, has been the neutron detector spectrometer. Since the first detection of hydrogen, and potential water, by the NASA's Lunar Prospector, many other missions have confirmed this hypothesis that during the last year, 2009, and it seems to be more real then ever.

#### **2.3.2.1. First detections: NASA's Lunar Prospector mission**

Lunar Prospector was a simple and reliable spin-stabilized spacecraft. It rotated around its own central axis to control its orientation on the journey to the Moon. Prospector was small and light (295kg when full). It carried small payload of only five instruments: gamma ray spectrometer, magnetometer, Doppler gravity experiment, alpha particle spectrometer and the neutron spectrometer; this last one is in charge of looking for water ice on the surface of the moon, by detecting hydrogen on it.

## Neutron Spectrometer

This instrument was on board specifically to detect and search water ice. [NASA Web Page, 1]. Since every water molecule contains two atoms of hydrogen and one of oxygen, hydrogen is a good marker for water, this is why neutron spectrometer is interesting for us, because it not only detected water, it allowed to determine the quantity of hydrogen and the distribution of it on the surface.

However, the NS did not detect hydrogen directly, since it was 100 km above the Moon's surface. Instead, it looked for what is called "cool" neutrons which are neutrons that have bounced off a hydrogen atom somewhere on the lunar surface. When cosmic rays collide with atoms in the regolith, they get out neutrons and other subatomic particles, like gamma rays. Some of the neutrons escape directly to space, as hot or "fast" neutrons. Other neutrons shoot off into the crust, where they collide with other atoms. If they only run into heavy atoms, they do not lose very much energy in the collisions, and are still travelling at close to their original speed when they finally rebound into outer space. They will still be warm (or "epithermal") when they reach Lunar Prospector and are recorded by the NS. Hydrogen is not a heavy atom, in fact it is the lightest, so the NS detect that they are those 'cool' neutrons.

### Results of the neutron spectrometer:

It was thought that there should be 10 to 300 million metric tons of water ice stuck in permanently shadowed craters at the lunar poles.

However, NS estimates were 3 billion metric tons of water ice at each pole. At the beginning, those estimations were based on the detected dips in medium energy or epithermal neutrons (see also figure 2.9) to see the distribution of these neutron on the entire moon) at the two polar regions (see figure 2.8). These dips of 4.6% for the North Pole and 3% for the South Pole remain essentially unchanged. The additional accuracy comes from an analysis of "fast" neutron data which indicates deposits of pure water ice hidden under around 50 cm of dry regolith.

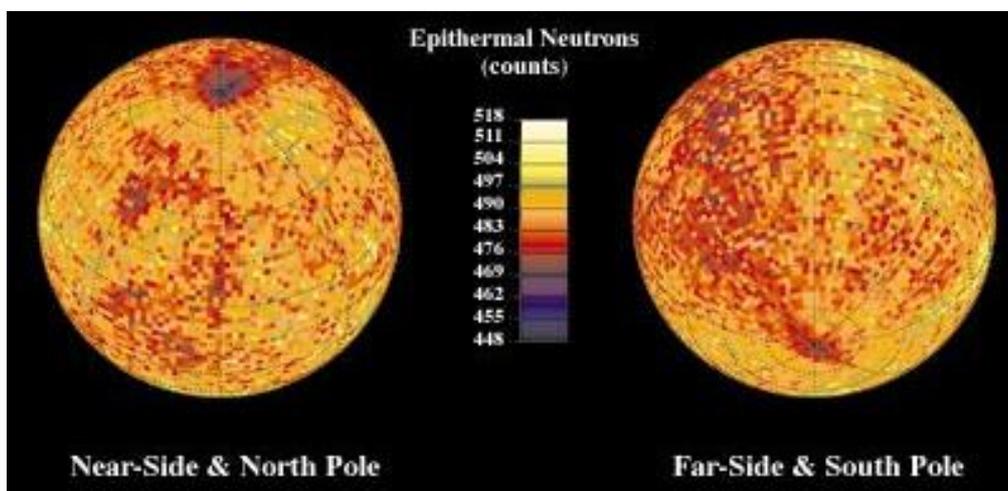


Figure 2.7. Distribution of medium energy (epithermal) neutron, which are a sign of hydrogen content [LP data].

The left side globe in figure 2.7 is the near side of the Moon tipped to show the North Pole. The dark purple region shows the dip in the neutron signal at the pole which indicates an excess of hydrogen. The "extra" hydrogen indicates the water ice at the Moon's poles in permanently shadowed craters. The right side image shows the far side tipped to show the South Pole.

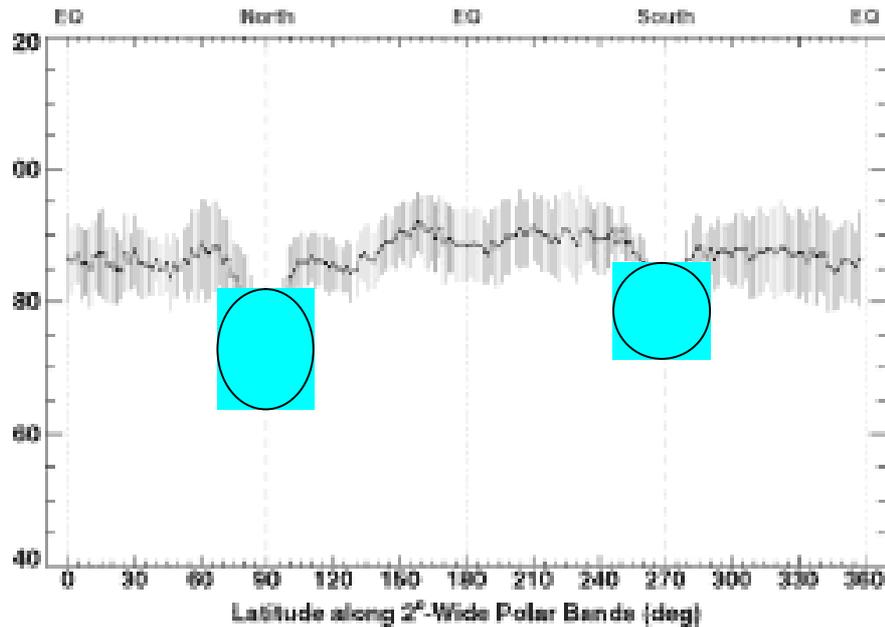


Figure 2.8. Medium energy neutron counts (LP data) showing the two polar dips which indicate water ice. Courtesy by Los Alamos National Laboratory.

The North Pole region, in particular, shows evidence of water deposits in permanently shadowed craters as you can see in figure 2.10.

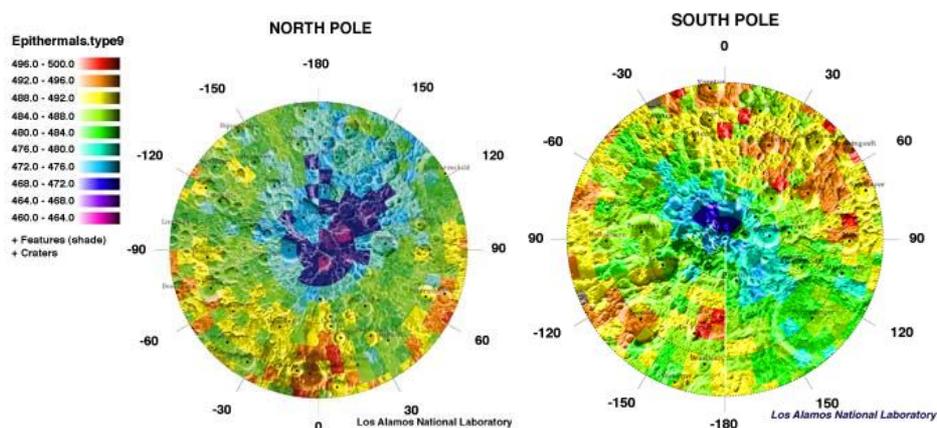


Figure 2.9. LP Neutron Spectrometer data from the North Pole and South Pole showing evidence of water ice (dark blue to magenta).

The NS instrument aboard Lunar Prospector could detect hydrogen to a depth of a half-meter. However, since the lunar soil has been effectively changed to a depth of two meters by meteoritic impacts over the past two billion years, the water could

theoretically be present to that depth if the water is in the form of ice crystals mixed with the regolith and even pure water-ice deposits could potentially exist at much greater depths. Recent missions such as ISRO's Chandrayaan and NASA's LCross targeted to impact on one of the pole craters to be able to remove those crust particles in order to analyze below the first centimeters of regolith.

### 2.3.2.2. Deposits of Hydrogen in the moon

The main deposits of hydrogen on the moon are known to be in polar zones; however, there are other areas such as permanently shadowed craters and equator zones with solar wind implanted and meteorites delivaration hydrogen.

Figure 2.10 shows a schematic distribution within the first 2 meters of the regolith.

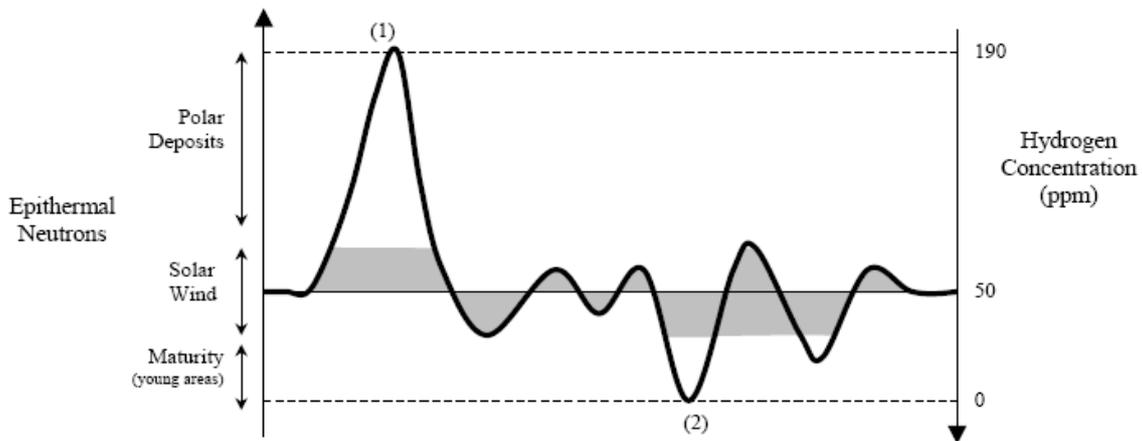


Figure 2.10. Grey part indicate the hydrogen concentration (around 50+-20) due to solar wind implantation. Lower points indicate dark craters like Tycho and higher ones are the hydrogen concentration at the polar areas (12 Hall Cutler, 1992). Maria have the lower concentrations of water, and at latitudes around the equator, the visual and infrared spectrometer carried by Cassini detects not molecules of water but hydroxyl molecules [Clark, 2009].

### 2.3.3. Estimation of Hydrogen in the moon

The hydrogen source is the most important element of the reaction, because it is the reductant. As mentioned in sections before, it should be brought from Earth but this is not feasible for long stays and for a continuous working Lunar Reactor Plant. The necessity to consider the Hydrogen as an in-situ resource is essential.

There have been several missions to the moon, and some of them detected a high evidence of the presence of hydrogen.

#### Cassini (ESA)

Cassini is a mission launched in 1997 with a main objective of landing on the surface of Titan, one of the 61 Saturn's natural satellites. However, during its way to Titan, Cassini did a fly-by of the Moon in 1999 and reported data from Visual and Infrared Mapping Spectrometer. It can detect water and hydroxyl molecules using OH and H<sub>2</sub>O absorptions (near 3 μm).

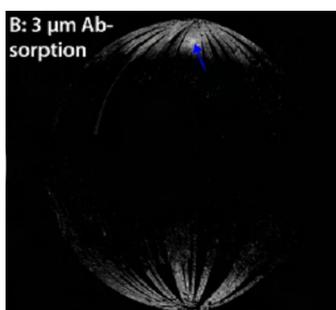


Figure 2.11. Cassini absorption map.

Some of the results obtained conclude that water is strongly hydrogen bounded and several minerals showed absorptions near  $3 \mu\text{m}$  and that the amount of water detected depended on if the regolith was mixed with rocks or only soil, and on the grain size [Clark, 2009].

### Deep Space Impact Spacecraft (NASA)

Deep Impact mission was launched on 2005, starting a 7 months travel to Tempel comet. It impacted on the comet to identify the composition of it. One of the most surprising data obtained by this spacecraft on his way to the comet passing very close to the moon suggests that our satellite is hydrated and dehydrated depending on some areas and on the daytime. The minimum hydration appears to be near noon; however the entire lunar surface is hydrated during at least some portions of the day, with a common maximum during night. This daily hydration and dehydration process may lead to a migration of OH towards the poles and its accumulation on the dark areas. The water content estimation is around 0.3wt% [Sunshine et al., 2009].

### Chandrayaan-1 (ISRO)

This first Indian mission to the moon was launched in 2008 in order to know more about our closest space body, especially to prepare a tridimensional atlas and to conduct a chemical and mineralogy map.

Abundance estimates were possible using assumptions about the physical form and location of the hydrated species. This modeled assumption suggests that the abundance can be as high as 770ppm, but it always depend on particle size [Peters et al., 2009, and ISRO web page]

### Lunar Reconnaissance Orbiter (LRO) and Lunar Crater Observation and Sensing Satellite (LCROSS) (NASA)

LRO was launched in 2009 with its main goal to create an atlas of the moon features and resources in order to get information for the future returning of the man to the moon. Like the Lunar Prospector spacecraft, this mission carried a neutron detector spectrometer (LEND) that will be able to detect deposits of hydrogen.

In addition, LCROSS will be launched in the same spacecraft, this part of the mission has the main goal to impact in a pole crater called Cabeus, (figure 2.12) in order to verify what NASA's Lunar Prospector suggested 10 years ago.

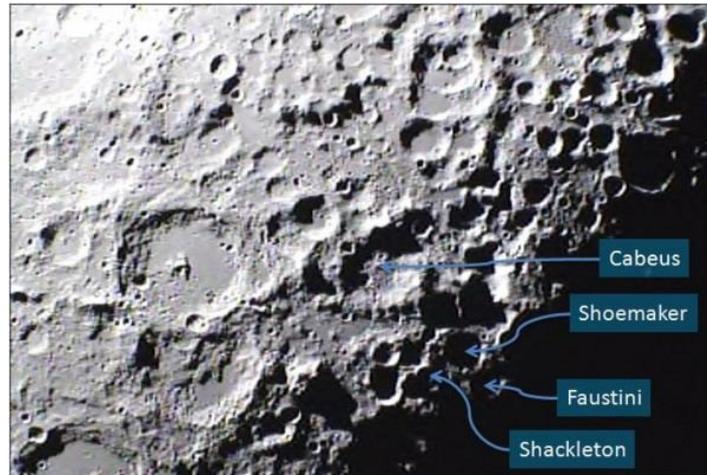


Figure 2.12. Detail of the target crater area, in the lunar southern pole. It is an area full of permanently shadowed craters. Some papers talk also about the Shoemaker or Faustini crater as ones that can hold huge quantities of ice. Image courtesy by NASA. [37 Zozlova and Shevchenko].

The data from these two missions are still under analysis by several scientists around the world, however the first results suggest that there is a high quantity of water cumulated on permanently shadowed craters on the poles. [NASA web page, 3&4]

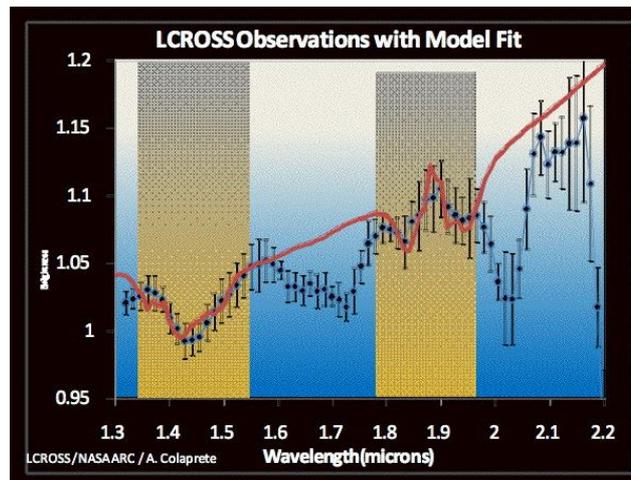


Figure 2.13. Infrared spectrometer data from LCross. The red curve shows how the spectra would look with water vapor and ice. The yellow areas indicate the water absorption bends. [NASA Web page]

### Lunar Prospector Neutro Espectrometer

The “Lunar Prospector” spacecraft, launched by NASA towards the Moon in 1998, was equipped with a neutron spectrometer for detecting possible deposits of volatiles in the polar areas of the Moon. In the region of the south pole of the Moon, maximum hydrogen content was found in the areas coinciding with such craters as Faustini (87,2° S, 75,8° E, D = 45 km) – 160,3 ppm and Shoemaker (88° S, 38° E, D = 56 km)

- 146 ppm. The average level of the contents of hydrogen for the Moon is around 50 ppm. [37 Zozlova and Shevchenko]

### Clementine Bistatic Radar

In 1994, the “Clementine” spacecraft launched by NASA explored the Moon for 70 days. As a result, a radar experiment made possible to discover areas with anomalous radar properties [Nozette et al., 1996]. It was detected an enhancement localized in some shadowed regions of the south pole (see figure 2.14), that did not appear on the illuminated areas. This was attributed to low-loss volume scatterers, such as water ice.

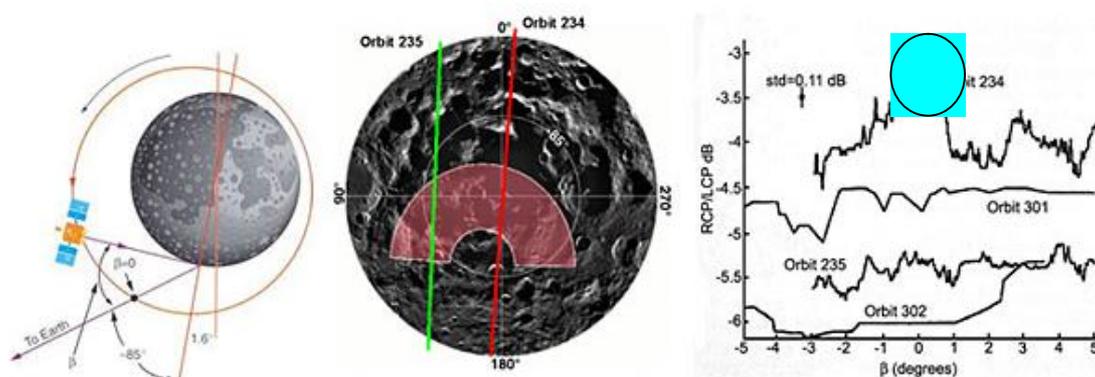


Figure 2.14. The figure shows the orbits done by the Clementine spacecraft, as you may have noticed, orbit 234 which passed over the pole detect an enhancement at 0 degrees. [Nozzete et al. 1996].

## 2.3.4. Potential areas to find H<sub>2</sub>O

### 2.3.4.1. Shadowed Areas

All the missions explained in previous sections, specially the oldest ones suggested more than ten years ago that if there was water on the moon it would be in the dark areas. Elphic [Elphic et al., 2005] said that the actual abundance on and under the surface depends on the areal distribution of this permanent shadowed areas, including the small craters too.

The lunar surface is illuminated when the solar altitude is different to zero and when all the elevations until 210km in solar irradiance direction are lower than the critical elevations [11 Li at al., 2008]. In addition, the fact that the Moon's axis of rotation is inclined at only 1.6° from the normal to the ecliptic, as shown in figure 2.15, means that permanently shaded regions exist inside many craters within 10° of the lunar poles. These regions should be sufficiently cold (<100 K) to prevent significant sublimation of water ice over billions of years [41 Eke at al., 2009]. In some craters the concentration of hydrogen is sufficiently high that it corresponds to around 10wt% water.

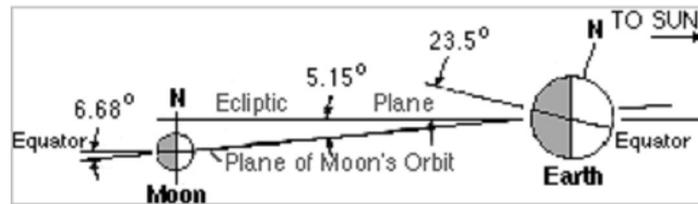


Figure 2.15. This diagram shows the final inclination with respect to the ecliptic, to its own orbit plane and to the Earth. [Spudis, 2006]

Shevchenko and Kozlova [37 and 27 Shevchenko and Kozlova], estimate the total permanently shadowed area in the northern polar region as 28260.2 km<sup>2</sup>, and in less quantity, about 22168.5 km<sup>2</sup>, in the region of the lunar south pole. According to their results, the total permanently shadowed area in the polar craters of the Moon is equal to 0.13% of the total area of the lunar surface.

Temperature on those shadowed areas makes water-ice deposits remain stable for a long time if the maximum temperature does not exceed 110 K. The temperature limit increases to 130-150 K in the presence of regolith. And sulfuric compounds remain stable if the maximum temperature does not exceed 220K.

This is that permanent shadowed area should be sufficiently cold to prevent sublimation of water [23 Andreas, 2007]. The shaded polar craters temperatures are being estimated to be around 40K; ice is stable at very low temperatures (less than 100K) and for temperatures below 70K, the sublimation rate of an exposed iced surface is less than one molecule of water vapor per square centimeter of surface per hour, (figure 2.16).

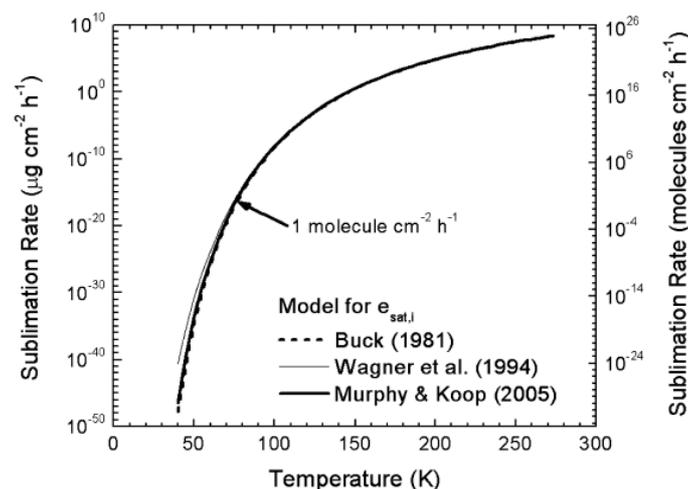


Figure 2.16. The sublimation rate for a planar surface of pure ice. (Right axis: sublimation rate as the number of molecules of water vapor leaving a square centimeter of the surface per hour. Left axis: sublimation rate as a mass flux) [Andreas, 2007]

In addition, ice deposits on the Moon might be “dirty” (mixed with regolith dust, carbon dioxide, or some other contaminant) and any of those contaminants will lower the saturation vapor pressure of the ice and, consequently, slow its sublimation rate.

## 2.3.4.2. Regolith

### Solar Wind Implantation

The hydrogen found in the regolith has its origin in the Solar Wind implantation, as explained in previous sections. This is because solar wind is mainly formed by hydrogen and Helium, and Ilmenite easily retains these elements.

### Meteorites, Asteroids and other space bodies... deliviration

Several comets and meteorites have bombed the surface of the moon over the whole life of the Solar System. The direct consequence of this is not only the small sticky particles of which the regolith is formed but also the amount of water reaching the Moon via these impacts, as well as the consequently migration of molecules to the polar 'cold traps' should be significant [39 Starukhina, 2000].

Lunar Prospector neutron spectrometer's signal can penetrate a depth of 5 meters, assuming this, Binder and Feldman estimate that the water ice on the moon would be in the range of 11 million to 330 million tons (10-300 million metric tons). This quantity is dispersed over 10000-50000 square kilometers of water ice in deposits across the northern pole, and an additional 5000-20000 square kilometers across the southern polar region. In addition, around twice of the water ice mixture was detected by Lunar Prospector at the Moon's North Pole compared to the south. [Morse et al, 1998]

In next figure (2.17 and 2.18) it is easy to distinguish the high concentration on poles, in higher quantity in the north pole, but not only in polar region but also in mid latitudes, due to this solar wind and micrometeorite impacts.

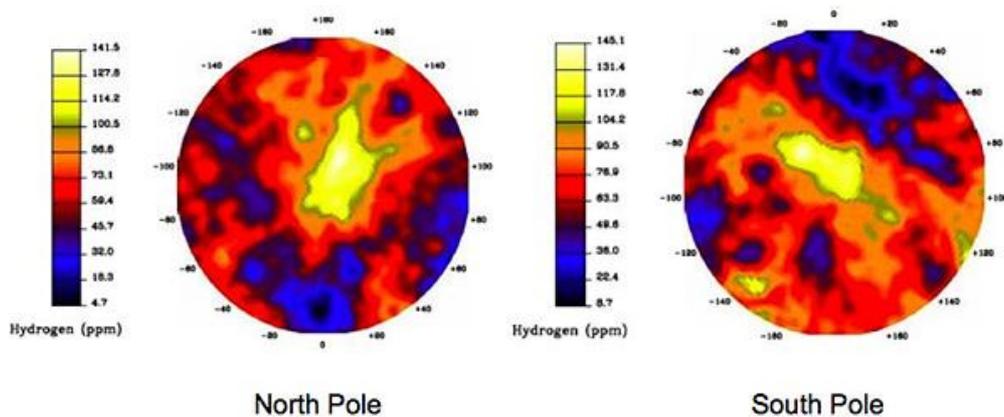


Figure 2.17. Lunar Prospector neutron spectrometer maps of the lunar poles. These low resolution data indicate elevated concentrations of hydrogen at both poles; it does not tell us the form of the hydrogen. Map courtesy of D. Lawrence, Los Alamos National Laboratory. [Spudis, 2006].

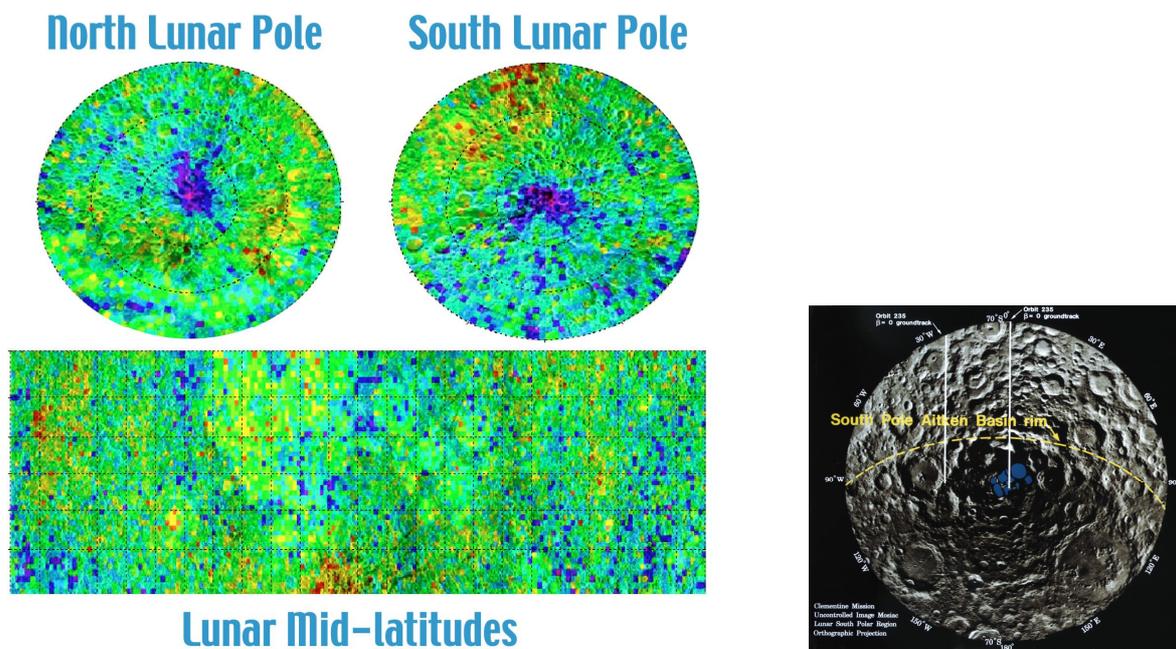


Figure 2.18. Left: map of the moon showing not only the poles hydrogen concentration but also the mid latitudes. Right: South pole with ice marked in blue

### 2.3.5. ESTIMATION REQUIREMENTS

A very accurate and exact estimation of the hydrogen and water content in the moon is not already done, as explained before there are several indicators of this high quantity and there have been done several estimations, however the scientific community is not unified on this. Some of the parameters are common and all the space agencies accepted as a verifiable fact such as that the major quantity of hydrogen is known to be concentrated on the poles of the moon. In the next table 2.5, some variables have been identified and summarized as the ones needed to do a good estimation of hydrogen and water content on the moon.

| Fact   | Lunar Value                           | Comments   |
|--|---------------------------------------|--|
| <b>Inclination of the moon with respect to the ecliptic.</b> | 1.6 degrees of inclination.           | There are shadowed permanent areas due to the inclination of the moon from the normal to the ecliptic. |
| <b>Latitudes with permanent shadowed craters.</b>            | Within 10 degrees of the lunar poles. | The permanently shaded regions exist inside many craters within specific latitude.                     |

|  |  |   |
|--|--|---|
| <p><b>Geological formations</b></p>                  | <p>Craters and Mountains at elevation within 210km will be illuminated.</p>  | <p>The lunar surface is illuminated when the solar altitude is non-zero and all the elevations within 210km in solar irradiance direction are lower than the critical elevations. Otherwise it would be shadowed.</p>   |
| <p><b>Temperature and atmospheric conditions</b></p> | <p>Shaded Craters are at 40K.</p>  | <p>As mentioned before ice is stable at temperatures lower than 100K and for temperatures below 70 K, the sublimation rate is much less than one molecule of water vapor lost per square centimeter of surface per hour. The absence of atmosphere and winds is a cause of the almost inexistence of no erosion on the surface, which means the sublimation of water ice has been prevented over billions of years.</p> |
| <p><b>Depth of the water deposits</b></p>            | <p>It could be around 5cm or even deeper (up to 50cm or some meters) in some areas.</p>  | <p>The estimated depth of water ice deposits is very important. Unfortunately current technology is not available to certify the data at too much depth.</p>  |
| <p><b>Total shadowed area</b></p>                    | <p>It is only estimated the polar shadowed areas in 50428.7km<sup>2</sup>. However, a better and accurate data would be very useful.</p> | <p>The maximum infrared water abundances based on LPNS measurements and estimates of areas of permanent shadow are about <math>1.5 \pm 0.8</math> %.</p>  |

|   |  |  |
|---|--|--|
| <b>Regolith particle size</b>             | See table 3.3 and 2.4 (particle size and % hydrogen concentration)   | It is known to be inversible proportional to the content of hydrogen.                              |
| <b>Concentration of detected Hydrogen</b> | It is thought that there is a mean concentration of 1.5%. In some areas it can arrive until 10%. Some papers estimate this concentration in an average of 50ppm and others suggest that the maximum can be up to 770ppm. | The data is not very consistent and there is a wide range of values.                               |
| <b>Missions collected data</b>            | Neutron Espectrometer, X-ray spectrometer, etc.  | These are the main resource of useful data. New technologies and more reliable data should be got. |

Table 2.5. Summary of the main variable when estimating the hydrogen and water content on the moon.

### 2.3.5.1. Existing estimation of lunar hydrogen and water content

These are some quantified data of the Hydrogen on the moon:

- “Lunar Prospector, Neutron Spectrometer: 3 billion metric tons of water ice at each pole. “
- “There could be as much as 260 million metric tons of water ice.”
- “Scientists believe that as much as 200 million metric tons of water ice could be mixed in with the lunar regolith in shaded craters of the South pole of the moon. These ice deposits, if they exist, are now believed to lie within 5 cm of the lunar surface in concentrations of approximately 1.5 %.” [Lunar Prospector mission overview]
- “Current data suggest that as much as 60 million metric tons of water ice could exist at the North lunar pole. “

There are other estimations done apart from the ones mentioned above, and almost none of them arrived to the same exact number. However, it is a fact that the order of magnitude of the quantity estimated by them is around hundred of millions of tons of water.

Polar Shadow Modelling: This model uses recent analysis of simple craters less than 20 km in diameter that yields estimates of approximately 500 and 6500 km<sup>2</sup> in permanent shadow for the north and south poles, respectively. Here they combine

the analysis of smaller craters with permanent shade, the north pole radar map, and illumination derived from Clementine imagery to construct two possible shadow models, one with a conservative shadow area totaling 5020 km<sup>2</sup>, and another more liberal shadow model with 26,100 km<sup>2</sup>. For their purposes, these shadowed areas would be allowed to have more than 5 wt% H<sub>2</sub>O under a thin layer of desiccated regolith. Areas not in permanent shadow would be considered sunlit (at least part of the time), and would only be allowed to have no more than 330 ppm hydrogen.

Fluxes of fast and Epithermal Neutrons: Taking into account, not only the immediate surface of the regolith but a depth of about 40 cm, this estimation has been done. These deposits would then have total effective surface areas of about 1850 km<sup>2</sup> at both poles. i) The ice deposits are below a 40-cm-thick layer of dry regolith, (ii) they are pure water ice, (iii) they reach a depth of 2 m, that is, the depth estimated to be turned over in 2 billion years, and (iv) the surface area of permanently shadowed crater deposits is 1850 km<sup>2</sup> at each pole as simulated. Then each polar region could contain as much as roughly 33109 metric tons of water ice. This amount is about an order of magnitude less than that predicted as possibly delivered to and retained on the moon by comets over the past 2 billion years. [15 W.C. Feldman, 1998]

Estimation of the concentration of trapped hydrogen in a mixed regolith layer in illuminated regions of the moon: One way to determine the hydrogen trapped in the surface of the moon is with the calculation of the saturation limits.

The model tries to analyze and compared if the Hydrogen on the moon is water ice or chemically trapped water. The lunar surface is exposed to bombardment by energetic protons that produce the formation of hydroxyl groups in the lunar regolith.

The model proposed to estimate the concentration of Hydrogen on the lunar regolith. [Starukhina et al., Y.G. 2000]

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## 3. STATE OF THE ART

### 3.1. Lunar Ilmenite

Hydrogen is present on the moon; the exact amount is not quantified yet as explained in the previous section, but there are several evidences of where to find it. The hydrogen may be extracted from the lunar surface, although for the first years the earth-resupply is needed. On the reactive part of the chemical reduction there is Ilmenite ( $\text{FeTiO}_3$ ). Characteristics of the ore mineral, where to find it, quantities on the moon and other issues are very important to know which will be the expected behavior of our reaction.

#### 3.1.1. Ilmenite on Earth

Ilmenite can be found on many places around the Earth. Its name come from the Ilmen mountains in Russia, however the major mines of the mineral are in Australia, Canada, South Africa, China and Norway.

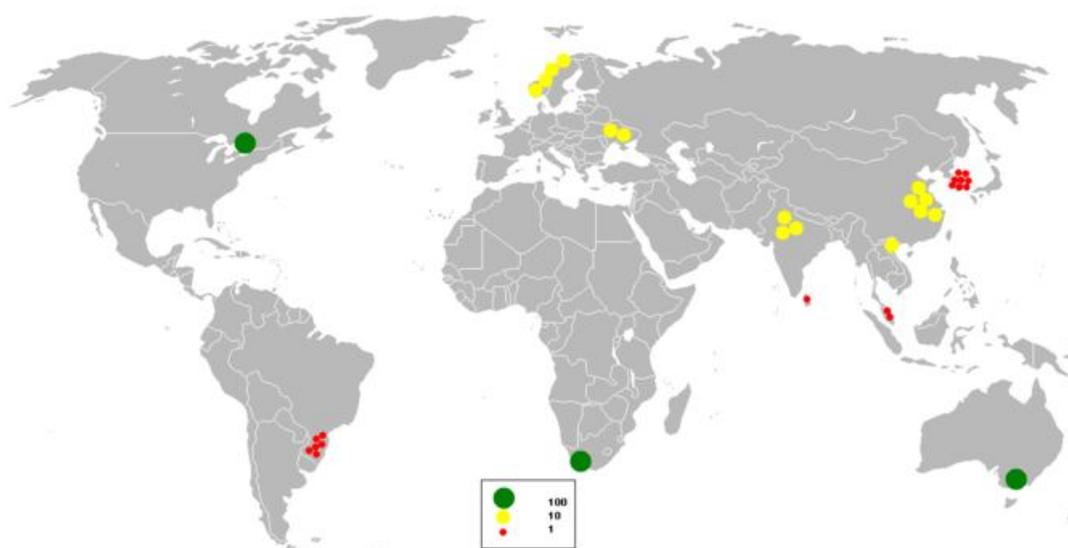


Figure 3.1. Ilmenite output in 2005 shown as a % of the top producers on Earth.

Although some scientists criticize that using terrestrial analogues for lunar experiments is not convenient and useful, many other experimental results suggested that the data obtained from this works with terrestrial samples is enough and valid to understand the potential behavior of the same analog materials on space. You can see its similarity between lunar and terrestrial ilmenite in figure 3.2. Anyway, there is less of 400Kg brought from Apollo missions and this material is not currently available.

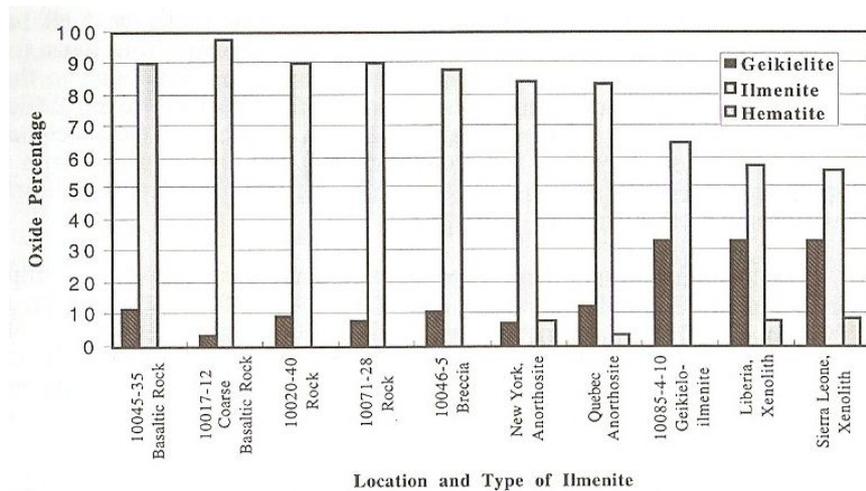


Figure 3.2. Mineral content of ilmenite samples. The terrestrial samples are very similar to the Apollo, except for a small amount of hematite. [Harris-Kulman and Kulcinski G, 1998]

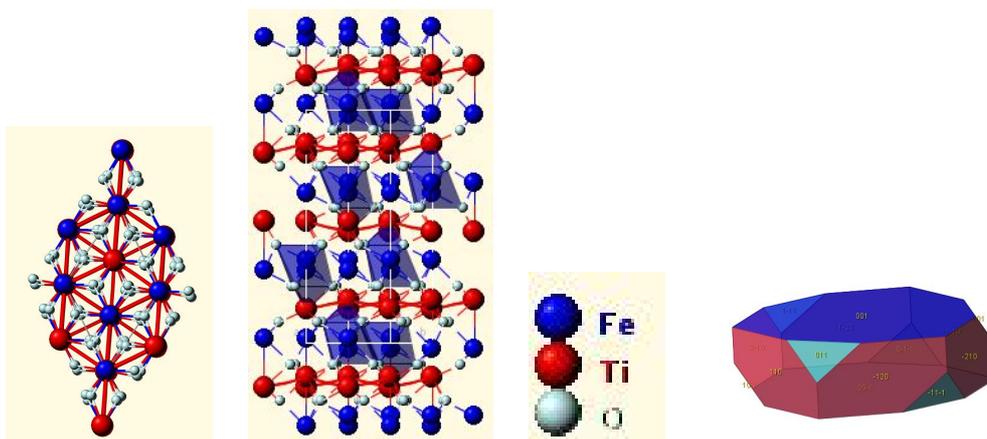
However, understanding the type of mineral on Earth and comparing it with the one from the moon is essential to determine which could be the main differences, not only on the reaction in itself but also on the future behavior.

The general chemical formula of the ilmenite is  $\text{Fe}^{++}\text{TiO}_3$ , with a molecular weight of 151.73mg, and a composition summarized on the following table (Table 3.1):

|                 |           |                       |
|-----------------|-----------|-----------------------|
| <b>Titanium</b> | 31.56% Ti | 52.65% $\text{TiO}_2$ |
| <b>Iron</b>     | 36.81% Fe | 47.35% FeO            |
| <b>Oxygen</b>   | 31.63% O  |                       |
| <b>Total</b>    | 100%      | 100% Total oxide      |

Table 3.1. Composition of pure Ilmenite

Ilmenite has a crystalized structure with a form  $(110)(011)(001)$ :



Forms:  $(110)(011)(001)$

Figure 3.3. Terrestrial Ilmenite structure

In the figures above, you can see its structure, and the position of the elements on the molecular net. Next table 3.2 shows the general properties of the terrestrial ilmenite.

| Cleavage                  | Color           | Density     | Diaphaneity    | Fracture  | Habit   |
|---------------------------|-----------------|-------------|----------------|---|---|
| None                      | Iron Black      | 4.72        | Opaque         | Conchoidal, fractures developed in brittle materials carachterized by smoothly curving surfaces | Massive-Lamellar, fine-grained forms or tabular |
| Hardness                  | Luminiscence    | Luster      | Magnetism      | Streak  |   |
| 5-5.5 Apatite-Knife Blade | Non fluorescent | Submetallic | Naturally weak | brownish black  |   |

Table 3.2. Properties of terrestrial ilmenite

### 3.1.2. Ilmenite on the moon

Ilmenite is chosen over the silicates to do the reaction, although silicates are considerably more abundant than Ilmenite on the moon, the silicates present higher difficulties on the process because they must be treated at least at 1100°C. However, Ilmenite can be reduced at temperatures below 1000°C and can be separated and concentrated from a natural abundance of 5 wt% to 90 wt% in the process feedstock [Gibson and Knudsen, 1988].

Ilmenite containing 32 percent titanium and 37 percent iron can be concentrated from some mare soils where it is present in amounts up to 10 percent. Ilmenite is also considered to be a commercial ore for producing titanium. It is most abundant in mare basalts, and soil is a better Ilmenite source compared with rocks. Regolith has the advantage of being easy to mine and because it is being already pulverized.

However, some of the ilmenite is present in fine-grained intergrowths or rock fragments that cannot be separated from the rest of components without additional grinding, which should be avoided. Consequently, the total ilmenite available is reduced if the grinding wants to be avoided; it means that the grain size is a very important factor and it will change the availability of the mineral.

| Grain Size $\mu\text{m}$ | Ilmenite Percent |
|--------------------------|------------------|
| 45-75                    | 6.0              |
| 75-90                    | 3.3              |
| 90-150                   | 4.6              |
| 150-250                  | 3.3              |
| 250-500                  | 2.3              |

Table 3.3. Ilmenite abundance in a single mare soil (Apollo samples) as a function of grain size.

The most ilmenite-rich mare basalt from Apollo samples contains about 25 percent of available ilmenite, and in soil it is around 9 percent.

Lunar Ilmenite contains 31.6 percent titanium and 36.8 percent iron (table 3.4). An Ilmenite concentration on a high  $\text{TiO}_2$  mare soil could concentrate 5-10 per cent of the soil as 90 percent pure ilmenite concentrate.

| Chemical Component      | Weight percent |
|-------------------------|----------------|
| $\text{TiO}_2$          | 53.1           |
| $\text{FeO}$            | 43.7           |
| $\text{Al}_2\text{O}_3$ | 0.26           |
| $\text{Cr}_2\text{O}_3$ | 0.72           |
| $\text{MnO}$            | 0.33           |
| $\text{MgO}$            | 2.0            |
| $\text{CaO}$            | 0.18           |

Table 3.4. Chemical composition of ilmenite from the Apollo 11 site.

The ideal mining site must be near both an immature highland area and a more mature  $\text{TiO}_2$  mare area. This could be at the eastern margin of maria, such as Tranquilitatis.

### 3.1.3. Relation between Ilmenite and Hydrogen

The ilmenite concentrate may be rich in solar-wind derived hydrogen, it could contain as much as 1000-2000ppm hydrogen in the fine-grained ilmenite.

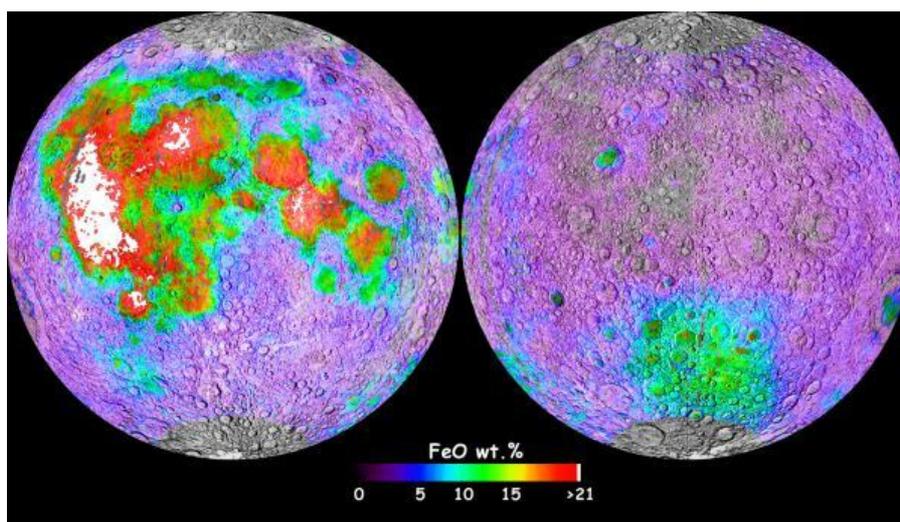


Figure 3.4. Map of the surface concentration of iron (expressed as FeO) on the lunar nearside (left) and far side (right), based on spectral reflectance measurements taken by the Clementine mission in 1994. The FeO data, from 70°S to 70°N, overlays a shaded relief map. High-FeO areas occur where volcanic lavas (mare basalts) filled giant impact craters. Low-FeO areas correspond to the feldspathic highlands. Image courtesy of Jeff Gillis.

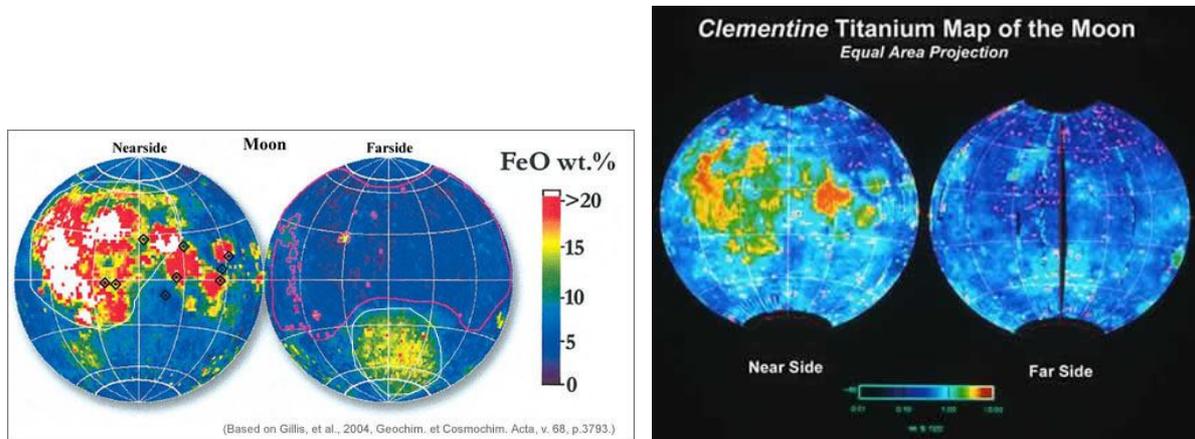


Figure 3.5. Titanium and Iron concentration on the Moon

The maps above (figure 3.5) shows the concentration of FeO on the Moon and the Titanium, as determined from Clementine data using a technique where low FeO translates into high  $\text{Al}_2\text{O}_3$ , consistent with the presence of lots of anorthosite.

As suggested before, the best place would be one near the mares in order to find ilmenite easily but also hydrogen, mare Serenitatis or Tranquilitatis could be good ones.

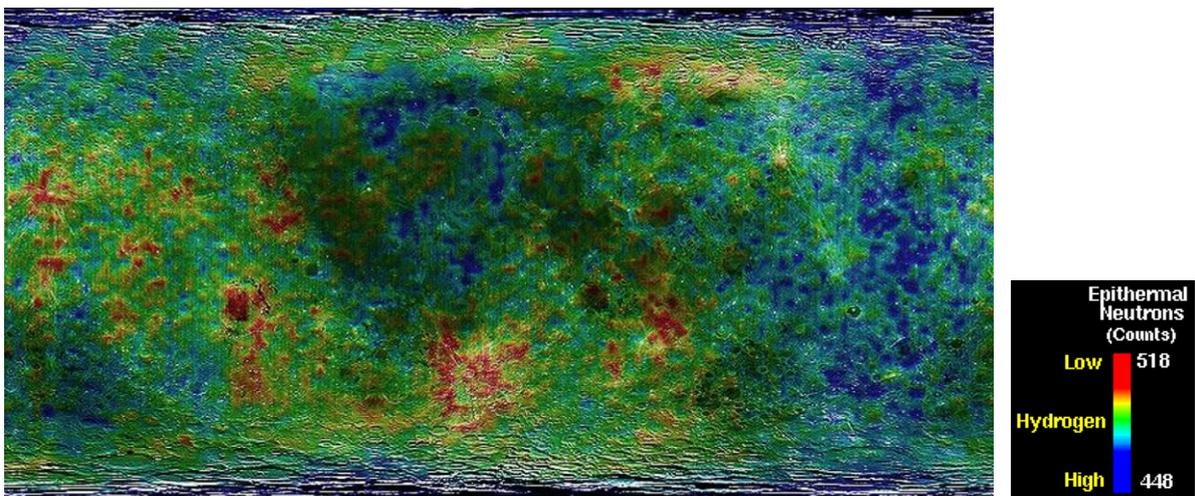


Figure 3.6. Blue areas are the major hydrogen content, as you may notice, areas right close to the Tranquilitatis and Serenitatis are blue colored

### 3.1.4. Differences between lunar and terrestrial Ilmenite.

The main difference is that minerals on earth solidified in more oxygen-rich environment than did those on Moon. Terrestrial minerals have been formed in the presence of water. Natural polycrystalline ilmenites from Sierra Leone, Liberia, NY and Quebec have been considered in previous studies [Harris-khulman et al. 1998], and compared with lunar samples.

Some of the most similar were analyzed by Harris-Khulman, they were from Canada, NY, Liberia, Sierra Leona...

The closest sample result was the NY sample, provided by Prof. John W. Valley of University of Wisconsin- Madison. The composition of this ilmenite was very similar to that of most lunar ilmenites with a small amount of hematite present.

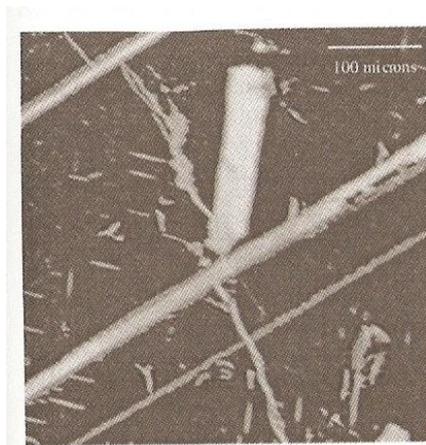


Figure 3.7. BSE image of Ilmenite from the Marcy anorthosite massif NY. The dark grey is ilmenite, and inclusions of Na, Al, Si, S, As, Ca and K are present

One of the samples analyzed during this thesis are the same as the ones analyzed by Harris-Kuhlman from New York; you can see its ilmenite component percentage and a BSEM Image of the sample (table 3.5 and figure 3.7).

| Chemical Composition           | Apollo 11 sample 10017-12 | New York sample |
|--------------------------------|---------------------------|-----------------|
| TiO <sub>2</sub>               | 53.95                     | 40.14           |
| FeO                            | 43.80                     | 40.69           |
| Al <sub>2</sub> O <sub>3</sub> | N/A                       | 0.00            |
| Cr <sub>2</sub> O <sub>3</sub> | 0.66                      | 0.02            |
| MnO                            | 0.40                      | 0.30            |
| MgO                            | 0.97                      | 1.99            |
| SiO <sub>2</sub>               | N/A                       | 0.33            |
| Fe <sub>2</sub> O <sub>3</sub> |                           | 8.03            |

Table 3.5. Composition of ilmenite grains of Apollo 11 samples and terrestrial samples.

On this study done by Kimberly R. Harris-Khulman & Gerald L.Kulcinski the conclusions were that the selection of a terrestrial analog lunar ilmenite is not a trivial exercise.

It is complicated by the difficult of the quantitative analysis of oxides and the fact that terrestrial minerals are grown in conditions different from the moon. The NY sample was chosen to minimize the effect of dissolved geikelite and hematite. This was the main reason to having asked for this kind of Ilmenite for our experimental part.

## 3.2. Ilmenite Reduction with Hydrogen

A small quantity of lunar soil has been returned to the earth in the Apollo missions, and as it was said in previous sections, the oxygen represents around the 60wt% of those samples [25 Horeland, 1998]. The key to obtain it in the desired state is to decompose that soil into pure elements; however, the energy needed to do it is a major concern. Among all the different methods to obtain oxygen the cheapest ones are those based on chemical reactions, such as the one assessed in this project: Ilmenite Reduction with Hydrogen.

The major minerals present in the lunar rocks that came with the Apollo's are Ilmenite (most abundant opaque mineral in lunar rocks), Anorthite and Olivine.

Extraction of oxygen from iron oxide is interesting because is energetically more favorable than extract it from aluminum, silicon, titanium, calcium or magnesium oxides. Actually, as was shown in the 2.3. Section, Ilmenite was a mineral used in a several number of them. The major problems of this reduction process are the necessity of condensate the water and to heat the H<sub>2</sub> necessary to have a feasible reaction; it means again enormous energy quantity.

This process was studied for the first time by Gibson and Knudsen in 1988. Briggs and Sacco (also in 1988) test the reduction of Ilmenite by hydrogen at 600°C and 800°C.

Carbotek (1988) developed a fluidized-bed reactor that makes the reaction at 900°C and 1000°C. Donnely (1970) showed that reducing the ilmenite grains and diluting the Hydrogen with CO decreases the rate of reduction of iron oxide. Zhao and Shadman (1991) experimented at the highest temperature [1014°C] with 3.4% H<sub>2</sub>.

### 3.2.1 Pros and Cons of the Ilmenite reduction compared with the others methods.

Another important analysis to be done to determine the feasibility of the process and to specify the main reasons of why it has been chosen as one of the best methods to obtain oxygen from lunar resources is the analysis of the advantages versus the disadvantages of the studied method. Moreover, in the *Processes to obtain Oxygen* section, different methods have been compared, including this one and the conclusions in that section said that the Ilmenite reduction with Hydrogen was one of the most feasible processes.

#### PROS:

- Chemical Process is not complicated and has been tested in laboratories [5 Eagle Engineering, 1988]
- The hydrogen is not consumed but recycled [25 Horeland, 1988]
- Ilmenite is present in Mare Rocks and solids and in Hi-Ti mares [20 Rosenberg, 1998].
- Temperatures needed are relatively low (around 900°C) for pure Ilmenites reductions [20 Rosenberg] and in any case they are below the melting point of the ilmenite feed which reduces reactor material problems.

- The technology to be developed is not a major problem [Taylor and Carrier, 1993]. It only must be addressed to reduce the plant mass and energy requirements.
- The process is only a 2 steps one, which decrease the probability of errors and mistakes, reduces complexity, increasing also the probability of low mass, reliable system.
- The process conditions are not very restrictive and the energy required is not too high.
- Resupply mass for reagent make up of process losses is expected to be small due to the low density of hydrogen gas.

### CONS

- Only Ilmenite is supposed to be reduced in this reaction, so to reduce the amount of the total handled material it should be separated from the bulk regolith.
- The kinetics for the hydrogen reduction reaction is relatively low (but not the lowest): 1 hour at 1000K is expected to be required to remove approx 70% of the oxygen associated with divalent iron in Ilmenite. Unoxidized ilmenite required 2 hours at 873K and 15 minutes at 1073K to completely reduce the iron oxide. The slower the kinetics, the longer and heavier a reactor must be for a given reaction temperature.
- The thermodynamics of the reaction impose fairly low equilibrium per-pass conversion of H<sub>2</sub> or H<sub>2</sub>O: 10.5% (molar) at 1000°C and 7% at 900°C. As per-pass conversion decrease, the reductant gas flow rate through the system must be increased for a given production rate, which then requires larger reactor and gas piping diameter.
- The main constrain is that large amount of regolith are needed to extract small input of gas, but it is quite simple to extract by heating. Other methods of extraction have been proposed such as microwave, microbial extraction... However, only a 0.02% is profitable from the regolith. (1 per each 2\*E<sup>4</sup> regolith), [Heiken et al, 1991, page 647]

### 3.2.2. Chemical process

This ilmenite reduction is a simple reaction that only has 2 steps. In the first step the reaction with Hydrogen to reduce FeO included in ilmenite, produces elemental iron and water; and the second step is just the electrolysis of the water [2 Hernandez and Franklin, 1992; and 19 Gibson and Knudsen, 1988]



At 900°C

$\Delta H = + 9.7 \text{ Kcal/gm-mol}$

Equilibrium H<sub>2</sub> Conversion = 7.4%

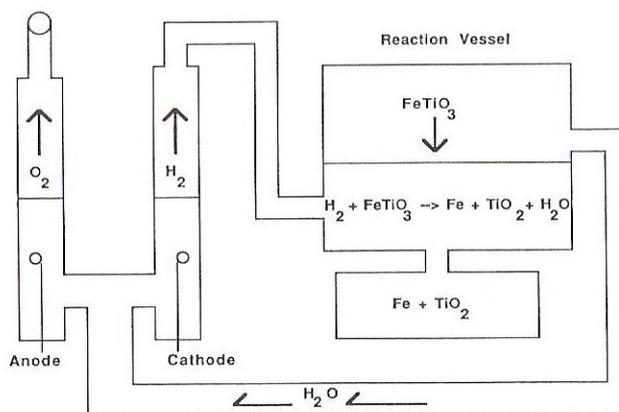


Figure 3.8 Ilmenite Reaction Vessel. [Hareland, 1988]

The quantity of Oxygen obtained should be only around 10wt%, it means that the rest 90% is removed. However, the hydrogen will be recycled during the process. It will be brought from Earth at least, during the first processes (then, it will be recycled), but it is not such a huge problem because  $H_2$  is one of the major propellants used and it has been brought from earth in almost every mission. (See figure 3.8)

### 3.2.3. Characteristics of the reaction

#### 3.2.3.1. Temperatures of reaction

This reaction becomes feasible from around 800°C. Ilmenite reduction is limited by the thermodynamics equilibrium, it means that the maximum limit depends on the tendency of the material to sinter into agglomerates which can interfere and even stop the reaction [2 Hernandez and Franklin, 1992].

The maximum temperature tested [33 Zhao and Shadman, 1993] has been 1014°C, demonstrating that there is an interphase resistance that starts to be important at higher temperatures.

Higher temperatures have been analyzed using plasma torches, microwave plasma and other similars to create such high temperatures, in a range of 3000°C and 6000°C. The results suggested that these greater temperatures will be required to dissociate the titanium from oxygen, while much lower temperatures will dissociate the iron from oxygen. It was demonstrated that the key to maximizing the recovery of oxygen will be to add a reactant (for example chlorine) that will react with Ti preventing the titanium from back-reacting with the oxygen.

#### 3.2.3.2. Equilibrium Conversion

The reaction's equilibrium improves with the temperature: at 900°C it should be around 7.4% and at 1000°C about 10% [2 Hernandez and Franklin, 1992].

#### 3.2.3.3. Product obtained

After the overall process, the ilmenite mined in order to have 1000 tones/year of Oxygen will be 40500 squared meters [2 Hernandez and Franklin, 1992].

### 3.2.3.4. Thermodynamics and Kinetics

Thermodynamics is one of the data that can change in a high way depending on the origin of the ilmenite (terrestrial or Lunar Ilmenite samples) [Gibson et al., 1992].

The kinetics of the reaction is good, which means that the time needed to finish the reduction is not too much. The slopes are almost lineal and proportional to the reaction rate, which is constant. The kinetics data can also be affected by the temperature and the pressure of the reaction rate.

Activation Energy is almost equal to the heat temperature and it is not very sensible to the temperature. The main effects of temperature gradient are on the equilibrium conversion attainable and on particle sintering.

### 3.2.4. COMPLETE PROCESS

The reduction of ilmenite in order to get oxygen from the surface of the moon is not dependent only in the reaction in itself; there is a complete process that begins with the collection of the crude ore from the rocks and soil, and end up with the storage and the utilization of the oxygen obtained (figure 3.9).

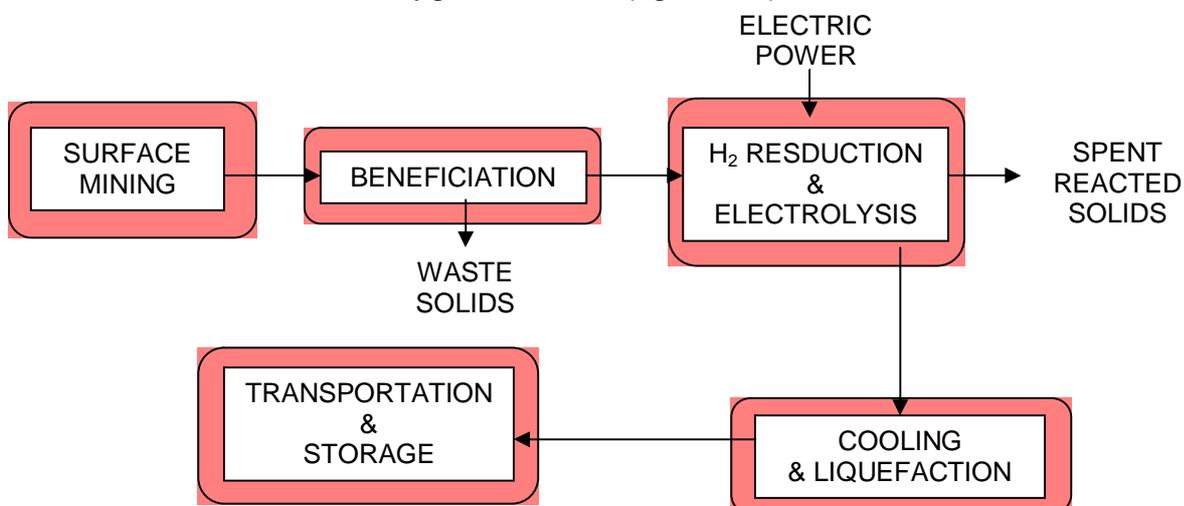


Figure 3.9. The complete Process, from mining to storage.

#### 3.2.4.1. Surface Mining

The mining of the lunar surface represent one of the major design problems, the main reason is the hostile environment. It is important to take into account the problems associated with a lower gravity, near perfect vacuum, temperature extremes, high radiation, bombardment of high-velocity particles and lack of gases and water. It is also important to not forget the geology of the base location.

There are different processes to consider: fragmentation, materials handling and processing. Each one of these steps would need different equipment and requirements [Sharp, W.R. et al., 1990].

The mining area, once a lunar base is established could consists of excavators, big and smaller ones, and haulers. The excavators deposit loads of basaltic rock in the

input bin. This could remove rocks larger than 10cm. Another container removes particles less than 1cm from the bin's undersize material [Eagle Engineering, 1988].

The systems that can be used on the lunar surface are already commercial available for terrestrial use and they are high level automotive; however, the need for maintenance and for operations suggests that the installation will be manned.

#### **3.2.4.2. Beneficiation**

Beneficiation is the process where the ore become a valuable mineral and useful resource. Preliminary steps in the beneficiation process are desegregation and size separation. Subsequent beneficiation might involve the separation of a nonmagnetic phase from a weakly magnetic waste, and ore with different density or electrical properties from ilmenite. [22 Williams, 1985 and Eagle Engineering, 1988]

#### **3.2.4.3. Ilmenite Reduction and Electrolysis and Cooling and Liquefaction**

Ilmenite is put through low and high pressure hoppers into a three-stage fluidized bed reactor (explained in the section 3.1.5). The mineral is preheated in the top of the bed reactor, reduction of Ilmenite by hydrogen takes place in the middle bed. Residual solids are cooled in the bottom of the bed and the water product from the middle bed is dissociated by electrolysis.

The oxygen is cooled, liquefied and stored while the hydrogen is used to preheat the incoming solids. Liquid hydrogen is vaporized to provide recovering for process H<sub>2</sub> losses. Active cooling loops transfer waste heat from other equipments to a central radiator system.

#### **3.2.4.4. Power**

Solar-electric sources can provide power during the lunar day for the process and for regenerating reactants used in fuel cell power storage systems. During lunar night fuel cells maintain high temperature. An alternative to this could be a nuclear-electric power source that would allow the process to operate day and night.

#### **3.1.4.5. Transportation and storage**

Storage is important because this is the last part of the process and the one that should maintain the product obtained during the whole process and during the stock. Storage tanks must be located in a kind of isolated place to avoid high gradients of temperatures and regolith filtrations, as well as in a ventilated area for security measures (oxygen is very inflammable) .

Transportation systems are not as important as storage because the storage tanks are immediately in the last step of the reactor, which means that almost no transportation from the reactor to the storage tanks is needed. However, rovers and conveyor belts could be the best option.

### 3.2.5. Ilmenite Processing Unit (IPU), Lunar Reactor

The main piece of equipment for an oxygen production facility would be a continuously operated-fluidized bed reactor which allows for direct contact between Ilmenite and Hydrogen. Secondary equipment, immediately after the reactor chamber would be an electrolyser [Eagle Engineering, 1988] to separate oxygen from the water molecules.

#### Reactor types

There are many types of reactor, which is needed to do the reduction. Four basic current existing designs valid for the reaction are defined; Roberto O.Ness concluded that the continuous fluidized bed reactor is the best option for this reduction [31.Ness, 1992]. It is called fluidized because it provides moderate heat transfer rates, temperature uniformity, high throughput rates, temperature uniformity, rapid mass transfer and mixing characteristics; and continuous because this kind of reactor can be oriented vertically with a stationary shell, or horizontally with a rotating shell. It allows a higher heat transfer rate. In the rotating one, the contact between solid and gas appears at lower pressure drops.

The design of the reactor depends on different factors such as size of the hooper, cyclone sizes, the H<sub>2</sub> contaminant removal standpipe sizes, predictions of particle entrainment rates, fluid-bed solids behavior, thermodynamics and kinetics for the hydrogen-ilmenite system, lunar specific environmental parameters... [Gibson et al., 1990]. After different analysis carried out the optimal 12500 mt/year ilmenite feed reactor system would consist of three stage of around 36 m length reactor, the diameter will varies between 0.65 and 0.80. The beneficiation of having a low gravity on the moon is that the particles are wider distributed.

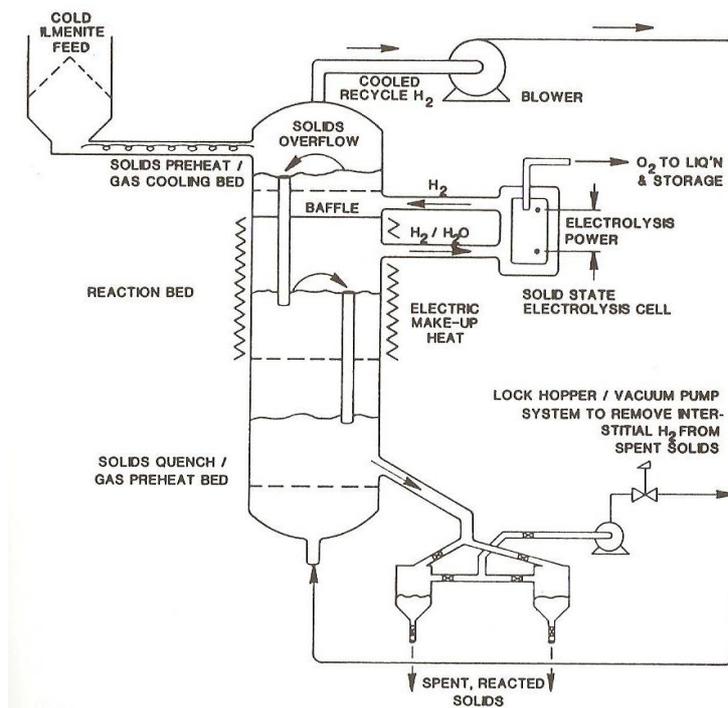


Figure 3.10. Continuous fluidized bed process for ilmenite reduction by Hydrogen [Gibson and Knudsen, 1988].

### 3.2.6. Experimental background results

Zhao and Shadman (1993) conducted a reduction of Ilmenite at the highest temperature ever tested of 1014°C with 3.4% H<sub>2</sub>. At this temperature the activation energy was around 22.3Kcal/mole. They also demonstrated that the interphase resistance is not important if the flow rate is at least 660std.cc/min and that at temperatures below 1014°C the interphase resistance is less significant.

An increase in the hydrogen concentration results on an increase in the rate and a decrease in the time required to attain certain fractional weight loss, which is defined as the ratio of weight loss of the sample to initial weight of the sample.

During the reaction at relatively low temperature are easily appreciable three stages: induction, acceleration and decelerations. (It does not happen at higher temperatures).

The rate reduction of titanium dioxide depends on both the Hydrogen concentration and the reaction time. It is important because 67% of oxygen in Ilmenite is bounded to Titanium.

There have been proposed some optimization to the reaction such as adding Co to the H<sub>2</sub> [Zhao and Shadman, 1993] adding Iron to Ilmenite or doing a preoxidation of the Ilmenite. Kinetics and efficiency are improved. (Figure 3.10)

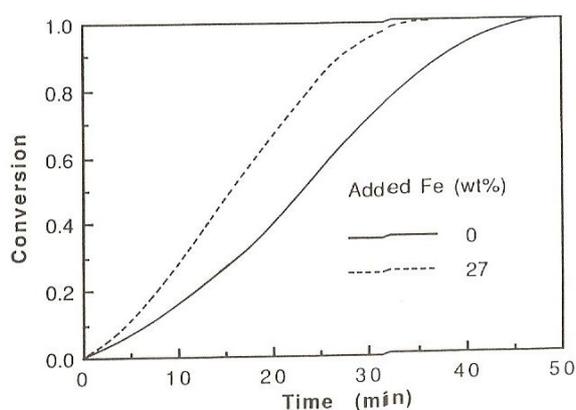


Figure 12. The effect of iron addition on the reduction rate of ilmenite. CO%=23, T = 1000°C.

Figure 3.11. Effect of iron addition on the reduction rate of ilmenite. Co=23%. T=1000°C.

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## 4. EXPERIMENTAL PROCEDURE

As stipulated on the project statement, the characterization of terrestrial ilmenite and comparison with the lunar ones will be done, but mainly in order to find the best sample to do the hydrogen reduction. Quantification of the oxygen during the reaction will give as the efficiency of the reaction, and we will be able to conclude about the feasibility of this process for future human settlements on the surface of our satellite.

In a general overview, the steps followed were:

- Obtaining the sample,
- Preparation for the SEM (Scanning Electron Microscope) analysis,
- SEM sessions,
- Preparation for the TPR (Temperature Program Reduction),
- TPR sessions and
- Extraction and evaluation of the data.

The main objectives of this section are to explain how the verification of the Ilmenite content in each sample is done, and to do an estimation of the element found in each one using the FIB-SEM and X-Ray diffraction. Afterwards, the TPR will be conducted to analyze the loss of water during the reaction.

### 4.1. Sample Selection and Preparation

Three different samples are used for the experiments, in order to get a better concept of the existing earth samples and its similarity with lunar ones

These samples are named as follow:

| Sample Name | Source          | Comments   | Picture   |
|-------------|-----------------|--|---|
| S1          | Snarum, Norway. | Rock. 22.151gm   |  |
| S2          | Not identified. | Powder.<br>Grain Size < 500µm<br>Contamination with Magnetite, and some traces of Mn, Zr and Nb. |  |

|    |   |  |   |
|----|---|--|---|
| S3 | Tahawas Lake,<br>Sanford,<br>Adirondack<br>Mountains, NY. | Two big rocks. 90<br>ADK-2<br>Basically ilmenite-<br>magnesite ore and<br>anorthosite. |  |
|----|---|--|---|

Table 4.1. Summary of the samples characteristics

S1 was got from the Expominer Feria in Barcelona. This sample is an Ilmenite mineral from Snarum region in Norway from a mineral collection.

Visually it can be described as a sample with at least 3 different minerals: a metallic black, opaque one, a white, vitreous glass and a last mineral which is glassy, lime yellow mineral. The high quantity seems to be formed with the black mineral, followed with the yellow and white one, growth in some parts, like incrustations to the black. The white and cristal mineral is thought to be quartz, and a yellow mineral, can be fluorite or sulphur.

S2 was obtained from Dr. Ignasi Queralt of the Institut de Ciències de la Terra Jaume Almera, already in powder. Some of the grains have a magnetic behavior, which can be an indication of a content of a considerably quantity of magnetite.

S3 is a granular sample from Tahawas, Sandford Lake in the Adirondack Mountains; it was provided by Professor John W. Valley of the University of Wisconsin-Madison. Two big rocks, with very well defined macro grains, that can be distinguish by naked eye.

These minerals should be prepared in order to have useful samples to be analyzed with SEM.

The specimen holder for the SEM has a maximum diameter of 2cm, so the pieces should be cut in order to be fitted in it. In order to cut S1, we used the saw 'Sierra de Precisión Isomet' 4000 from Buehler. Some aspects should be checked before starting the cut such as to make sure there is cooling liquid in the tank, place correctly the blade and tight all the screws very carefully.

A small cut was tried before doing the final one. Parameters were adjusted as follows: *blade speed* of 3000rpm, a *feed rate* of 4mm/min and a *cutting length* of 17'52mm. The blade used was a *diamond blade*, and all the parameters were selected according to a table enclosed with the equipment instructions.

The first cut was successful, so I proceed to do the final cut with the same parameters, now the cutting length was 17,27mm. This cutting length should be measured before starting the cut, placing the blade at the beginning of the sample, initializing the value (zero) and then moving the blade till the desired final point.

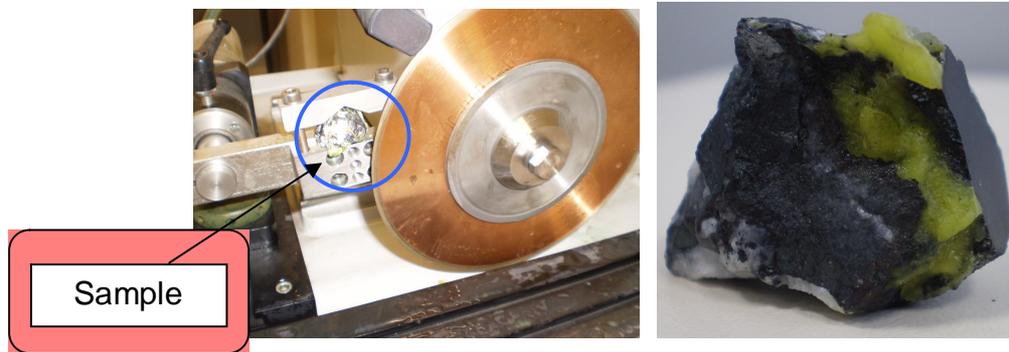


Figure 4.1. Left: cutter. Right: cutted S1.

Once the piece is cut, the next step is to polish. In order to do that 'Pulidora Phoenix 4000' from Buehler is used. Some requirements before using it to consider were to open careful the water pump and the pressured air bomb. A manual polish was done, so the option 'Head' should be in 'Off'. Cycles of 2min50sec at a speed of 300rpm were performed.

I started with the roughest sandpaper (7 cycles), then I started decreasing the grain size of the sandpaper, less roughed paper (10 cycles), sandpaper of grip800 (20 cycles) and finally a sandpaper of grip1200 (10 cycles). Each cycle was around 3 minutes.



Figure 4.2. Manual polish of the sample.

Once S1 was polished, a section in order to place it in the SEM specimen holder was cut using the same equipment as the previous cuts (Cutting length of 22.35mm). S1 was ready to be placed on the SEM specimen holder using carbon tape to fix it. S2 and S3 were pulverized and placed in smaller holders.



Figure 4.3. From left to right: S1, S2 and S3 placed on the specimen holders, ready to be analyzed with SEM.

Before placing them into the SEM, samples should be carefully cleaned using ethanol, it is important to always use gloves and forceps to manipulate them because the grease of the skin can affect the results. Afterwards samples were left about 12 hours inside a hermetic and dehydrated closet in order to dry them as much as possible because SEM equipment is very sensible to water and humidity.

First results were obtained using these samples, they will be showed and commented in following sections and in Annex A; however, we observed that the mineral was getting charged due to the electron scanning during the SEM session and a better sample preparation was suggested to avoid this effect and improve the results.

In order to have better samples to improve the results, a smoother polished should be performed and also a conducting line from the sample to the specimen holder was needed to avoid the charge of the sample.

In order to have a better finished on the surface of the cut, an automotive polisher was used. It allows doing more cycles in less time, more than one sample at a time, and the same vertical force is applied during the whole process.

Samples need to be mounted in an specific resin. It was done using Buehler Cast n'Vac Vacuum System, which is a vacuum impregnation system for use with castable. The resin selected was Epo-Thin (Epoxy resin), this has a ver low viscosity and the best penetration of voids during vacuum impregnation, it has a good adherence to the specimen and is highly recommended to use for minerals.

Preparation is very simple, the resin should be mixed (it has two main components) inside an specific cup, taking care of the way it is done to avoid to much air penetration. The proportion between both components of the resin is 39/100, for this reason they should be carefully weighted and filled the cup drop by drop, controlling the ratio. (see figure 4.4)

The minerals were placed at the bottom of a small vessel, the Cast n'Vast system did vacuum, and when it arrives to the desirable value of vacuum, the resin will enter to the vessel through epoxy supply tubes. This should be done very slowly. When the sample is completely covered, resin supply is stopped and the vacuum is taken out. The preparation should be dried during at least 9 hours at 27°C.

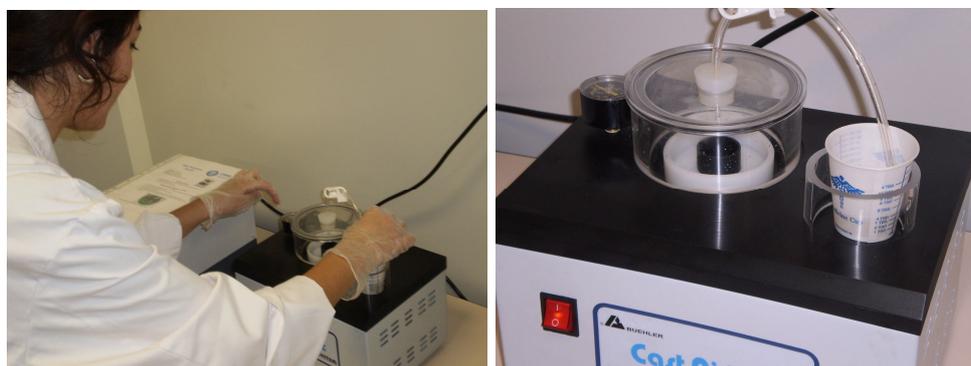


Figure 4.4. Preparation of the cast of the samples.

The final appearance of the samples are like in figure 4.5.

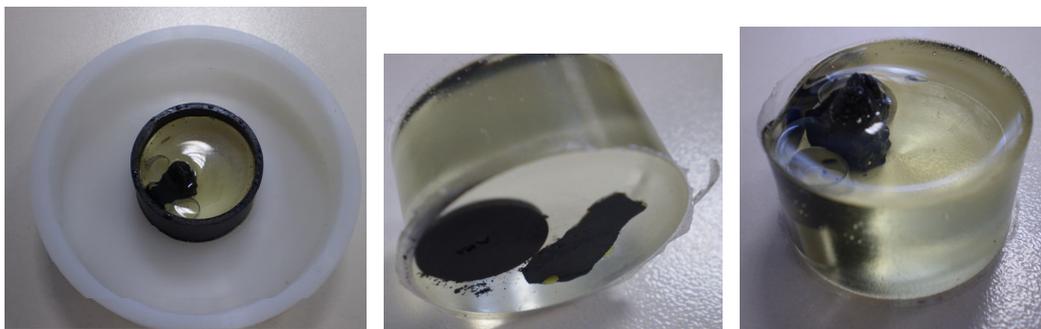


Figure 4.5. The transparent component is the already dried resin. Left image shows the sample during its drying, middle and right images show the samples placed inside the resin, ready to be automotive polished.

S2 is converted into a tablet, as you can appreciate on the picture above, it was needed because this sample was available in powder, so it was pressed before using 'SPECAC sample preparation press'.

Once the samples are ready, they can be fitted into the automotive polisher, using cycles of from 4 minutes to 15 minutes at a speed of 200 rpm. The sand paper will be changed to smaller grid size among the whole process. The surface become a very smooth one.

Finally, they were recovered with Carbon by 'Serveis Cientificotecnics UB', in Barcelona to avoid electron charging of the sample and silver paint was used as a connection with the sample to the specimen holder. (see figure 4.6)



Figure 4.6. Samples covered with the carbon, see that there are darkened; and the silver conducting line can also be appreciated.

## 4.2. Scanning Electron Microscopy (SEM) Study

Once the samples are ready, carefully I started using FIB-SEM SEM Shottky, 4pA-20nA, 0.1-30kV, 1.1nm of resolution equipment with the laboratory technician help. The equipment consists of three main chambers, with three different vacuum values that must remain always in the same order of magnitude: system vacuum around  $e^{-6}$ , Gun Vacuum around  $e^{-10}$  and FIB Vacuum around  $e^{-8}$ . These values should be checked during the whole process to make sure they are maintained during the whole session.

The specimens holders are screwed in the sample holder, bear in mind that the screws do not protrude the bottom of the holder; and it was placed inside the system chamber. Vacuum is maintained during the whole entrance performance. Samples are placed where desired using the joystick and the different controls on the keyboard. Voltage is adjusted (EHT 'ON' between 2kv and 8Kv, depending on the infrared energy emission of the sample) and SE2 activated. In order to extract concrete data from the images the software used is called INCA (X-ray mapping).

Three different SEM sessions were performed in order to obtain the most accurate and correct result. The first session was dedicated to understand how the software works, how to manipulate the commands and to extract the first rough data.

During the second session, samples were observed in a more detailed way and quantification data was extracted. For the last session, samples were better prepared, since a higher level of experience was achieved, to obtain a high resolution images and data.

Some data extracted from the first session shows that S1 has not a huge quantity of Ti, so it is thought that maybe is not an ilmenite specimen, or just in a very small quantity, but mainly a magnetite. However, S2 and S3 manifest great quantities of Ti, especially in some grains which are almost pure ilmenite, apart from other elements detected such as aluminum, manganese among others.

S2 should be analyzed more carefully, but S3 looks like could have huge and almost pure ilmenite grains. In order to see the ilmenite quantity distribution of S3 a general view of the sample was captured. Once ilmenite grains were identified we zoomed on them.

During the second session of SEM, the samples were observed in a more systematic and detailed way. Different areas of each sample were analyzed in order to have at least a general characterization and not only a specific area or grain which could not be a remarkable data of the overall composition of the sample. The main objective is to identify the purest ilmenite to do the hydrogen reduction and to characterize the terrestrial ilmenite and its purity in order to compare with the lunar ilmenite.

All samples were observed at a Working Distance (WD) of around 7.3mm, a magnification of 5000 and a voltage of 8kV. The voltage is selected considering the x-ray emission energy of the key elements (Table 4.2).

|          | K-alpha (eV) | L-alpha (eV)   |
|----------|--------------|----------------|
| Titanium | 4510.84      | 452.2<br>458.4 |
|          | 4504.86      |                |
|          | 4931.81      |                |
| Iron     | 6403.84      | 705.0<br>718.5 |
|          | 6390.84      |                |
|          | 7057.98      |                |
| Oxygen   | 524.9        | -              |
|          | 524.9        |                |

Table 4.2. X-ray emission energy. A voltage of 8kV was selected because as you can appreciate Iron energy is around 7thousand.

The maximum emission energy is the one from the Iron, which is around 6.5, so it was decided to select EHT= 8kV in order to avoid excess charging in the sample but at the same time be enough to detect the key elements.

The images and the quantified elemental analysis got from the SEM session can be seen in the Appendix A. Elemental analysis was done to distinguish the different elements found in each sample, specially looking at the detection of Titanium, Iron and Oxygen, in order to determine the purest sample.

We could say that S1 seemed not to be that much of ilmenite but more magnetite. In order to detect ilmenite in S2 and S3 composition, more accurate analysis were needed. In those two samples there were lot of grains and some of them were very different from others. For this reason, different areas of each sample were evaluated. All this results in a more detailed way and all the results found will be explained in Appendix A and section 5.

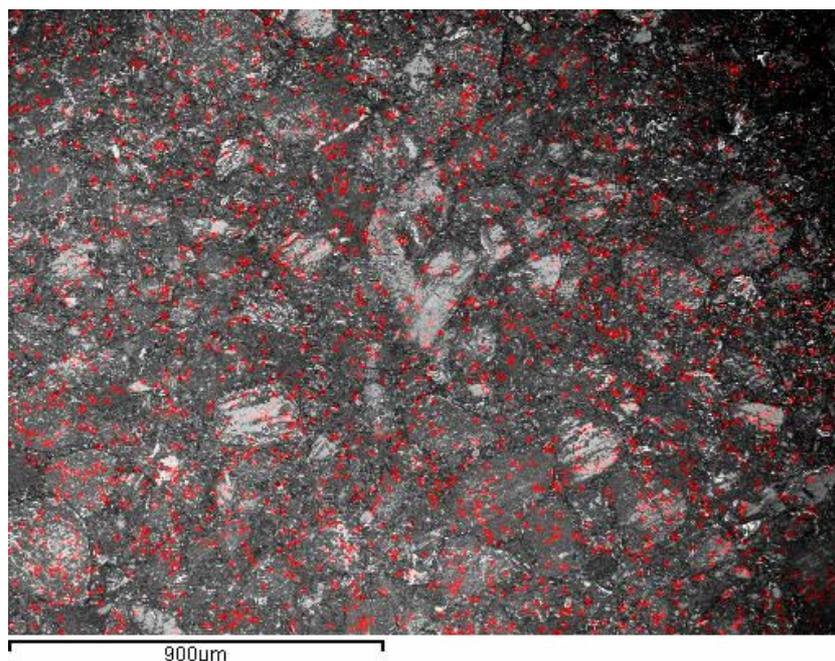


Figure 4.7. SEM image of S2 with Titanium marked in red.

### 4.3. X-Ray Diffraction (XRD) Study of a Magnetically Separated fraction of S2.

S2 needed a high verification on the mineralogical composition so an X-ray diffraction analysis was done. The sample was separated magnetically using a magnet to have a purer sample. I prepare the sample reducing the grain size (it was around 400 $\mu\text{m}$  at the beginning) using an Agate mortar (Figure 4.8).



Figure 4.8. Agate mortar

Figure 4.9 shows a comparison between the experimental results of a powder X-ray diffraction pattern of sample S2 (black) and a synthetic spectrum for ilmenite (red), as well as the difference (green) between both. The almost total coincidence between sample and synthetic patterns confirms that the sample analyzed is essentially pure  $\text{FeTiO}_3$ . The peaks enclosed in a circle (not belonging to the ilmenite pattern) are supposed to be contaminants in the sample. These contaminants could be Silica (the X-ray pattern shows an evidence of this) or (Nb, Mn...), although it is not very well defined when doing the analysis. However, it was possible to certify that no magnetite contamination was in this sample; probably due to this previous magnetic separation.

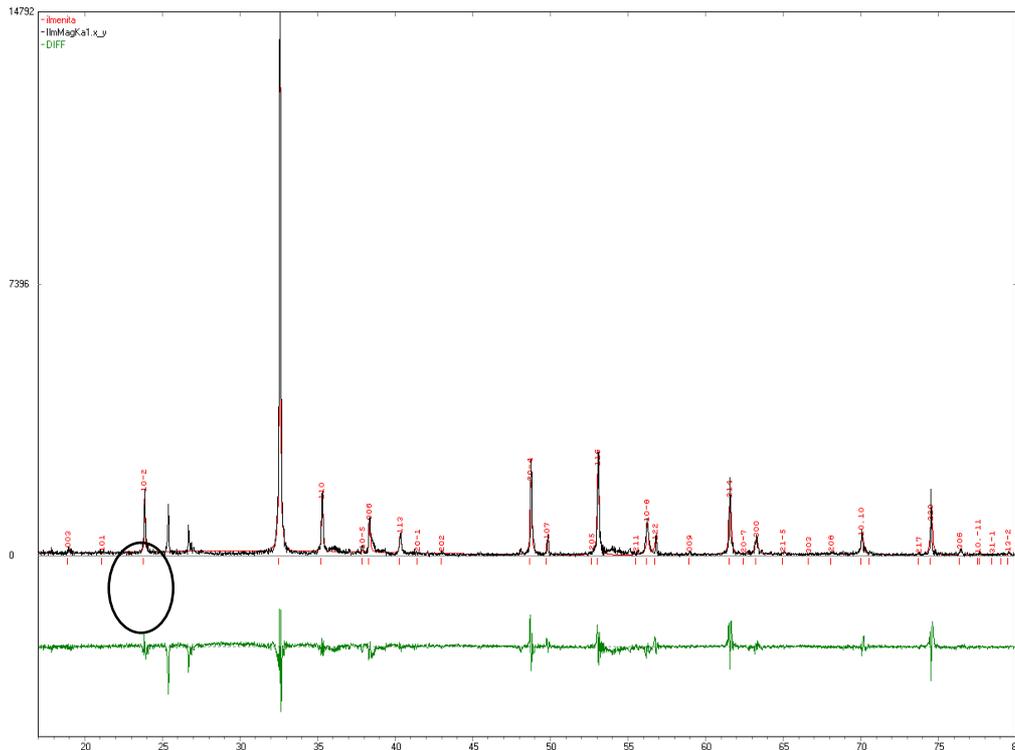


Figure 4.9. X-ray powder diffraction pattern of S2 ilmenite.

## 4.4. Temperature Programmed Reduction (TPR) Study

S2 was selected as the purest ilmenite of the three samples, so this was the one prepared for the TPR analysis. The Temperature Programmed reduction is a very high sensitive technique that consists of heating the element with a linear temperature ramp in a flow of hydrogen while monitoring the hydrogen consumption and the weight change in the sample, which is a direct consequence of the oxygen released as water. Smaller the grain size is, better results are obtained due to the specific surface, in previous sections it was already mentioned the importance of the parameter 'grain size'. Therefore, S2 was pulverized until having a very fine grain size and placed in small vessels to carry them.



Figure 4.10. Picture of the two types of grain (right: initial grain size; left: sample ready to TPR).

### 4.4.1 TPR Experiments

The TPR equipment used is a Perkin-Elmer TGA (Thermogravimetric Analyzer) 7 microbalance with an accuracy of  $1\mu\text{g}$ , equipped with a  $100\text{-}900^\circ\text{C}$  programmable temperature furnace. The equipment is placed in Serveis Tecnics at Universitat Rovira i Virgili in Tarragona. All the TPR sessions were conducted there at these facilities.

Sample was heated always first with pure Nitrogen ( $80\text{cm}^3/\text{min}$ ) in order to remove any contamination and to make sure that everything released by the reduction by hydrogen is due to the chemical reaction and not because of the some carbon or other contaminant reaction.

#### **TEST 1**

We heat the sample up to  $140^\circ\text{C}$  in order to make sure that any water or humidity is evaporated, and then cooled down again. Not too much loss of weight was observed, which is an indication that the sample is quite dry. This will make the experiment a little bit easier and will give more accurate results.

#### **TEST 2**

We heat the sample from  $100^\circ\text{C}$  to  $900^\circ\text{C}$  with Nitrogen gas as explained before.

The sample is heated from up to  $900^\circ\text{C}$  with a scanning rate of  $25\text{k}/\text{min}$  and a flux of  $1/20 \text{ H}_2/\text{Ar}$  and Nitrogen.

Data is saved in a .g7 file which can be read using .txt. Y, X columns is the format of the file. The Y value should be divided by 200 to get the %weight loss and X is the value of the temperature at each point.

In-situ observations suggest that the sample results may be quite accurate in terms of loss of weight per reduction, because it seems that no many contaminants are on the sample and that it is very dry, which means it has not lost weight during this first TGA; however, unexpected value appeared from 500°C to 900°C: the weight of the sample has increased a little bit, even going higher than 100% of the weight (figure 4.9).

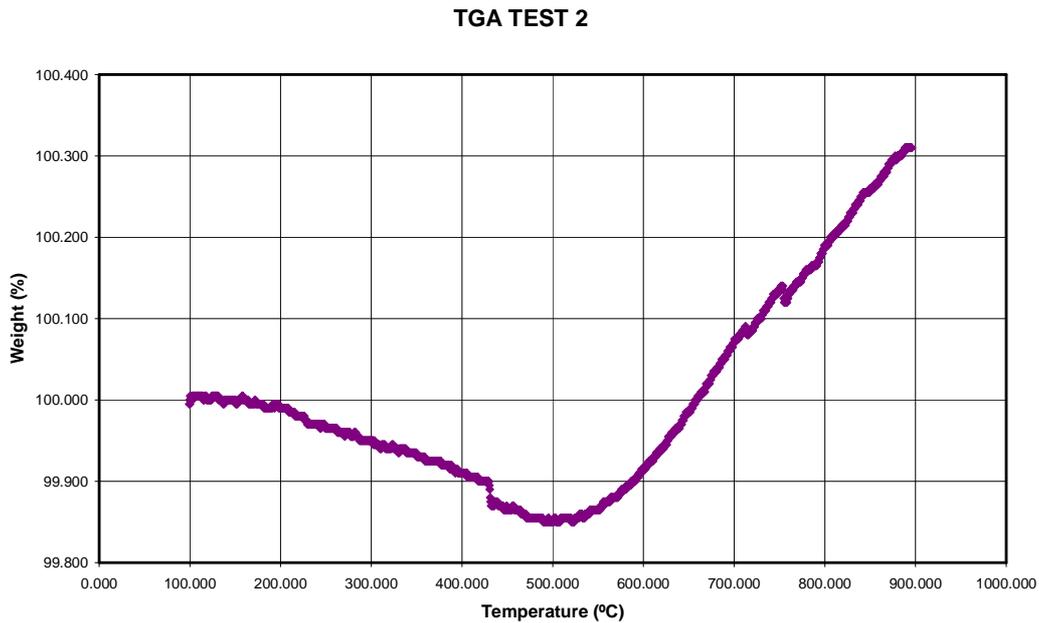


Figure 4.11. Weight% mass loss vs. Temperature during the preheat of the sample with N<sub>2</sub>.

### **TEST 3**

Afterwards, this sample, which we know for sure that everything released is going to be water from hydrogen reduction, was heated again now for the first reduction test.

Remember to open Hydrogen gas and make the entire process step by step (explained in Appendix B). This time, the same value parameters were chosen: from 100 to 900°C at 10K/min.

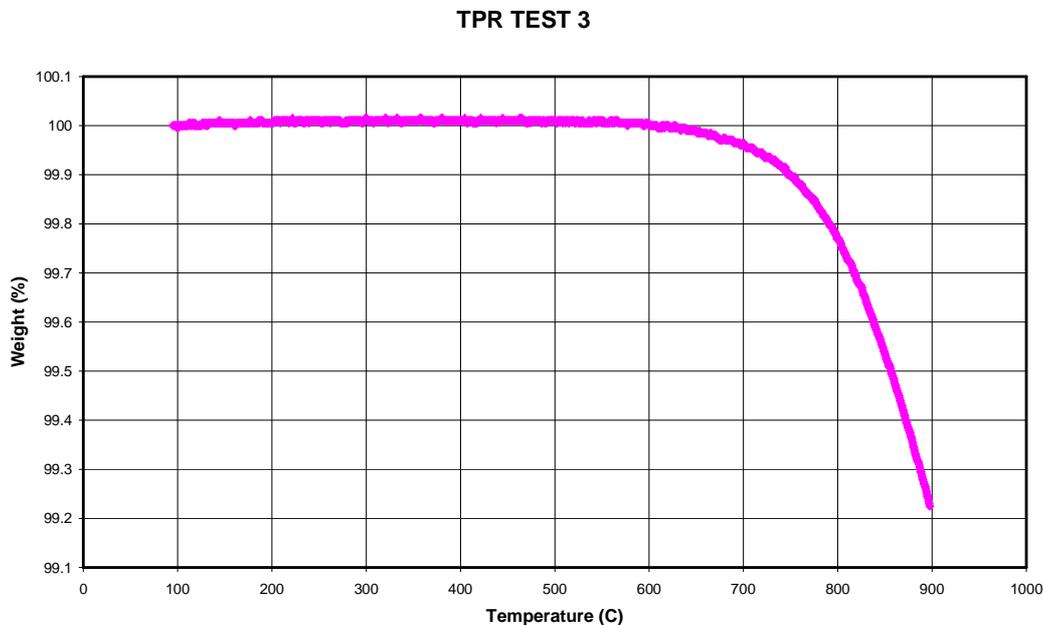


Figure 4.12. Weight% mass loss vs. Temperature at 10C/min.

#### **TEST 4**

This test was the preheating one by nitrogen, done at a scanning rate of 25K/min during 32 minutes. This is the pre-process before the next TGA.

The initial weight of the sample was 66.0923mg, and surprisingly it increased up to 67.521mg. However, it is appreciable a loss of weight up to 500°C, this is the evaporation of possible water humidity and other contaminants (see figure 4.11).

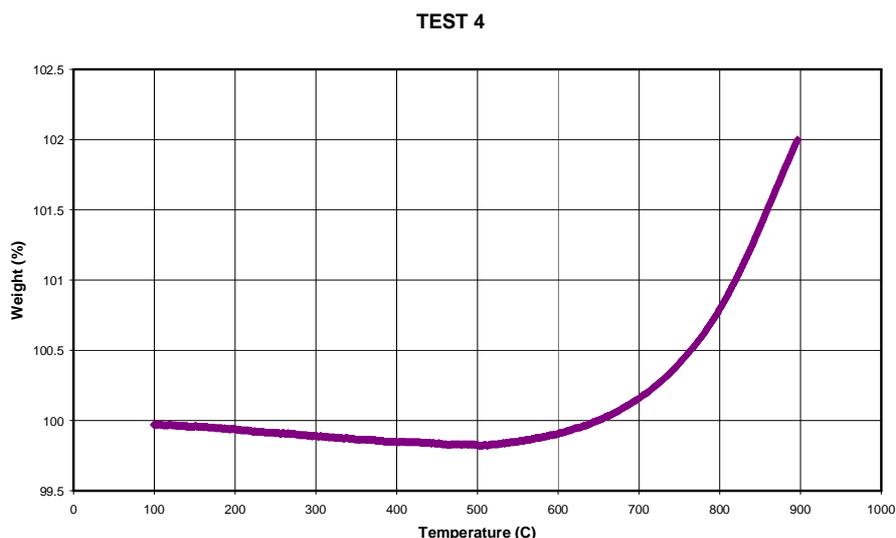


Figure 4.13. Weight% mass loss vs. Temperature during the preheat of the sample with N<sub>2</sub>.

#### **TEST 5**

After the TGA with nitrogen, hydrogen is connected. This time the TGA is done at a scanning rate of 10K/min which will last around 54 minutes until it achieve 900°C.

The initial weight of the sample was 67.521mg.

First in situ observations showed that a constant reduction process starts at around 700°C and it becomes faster at 800°C.

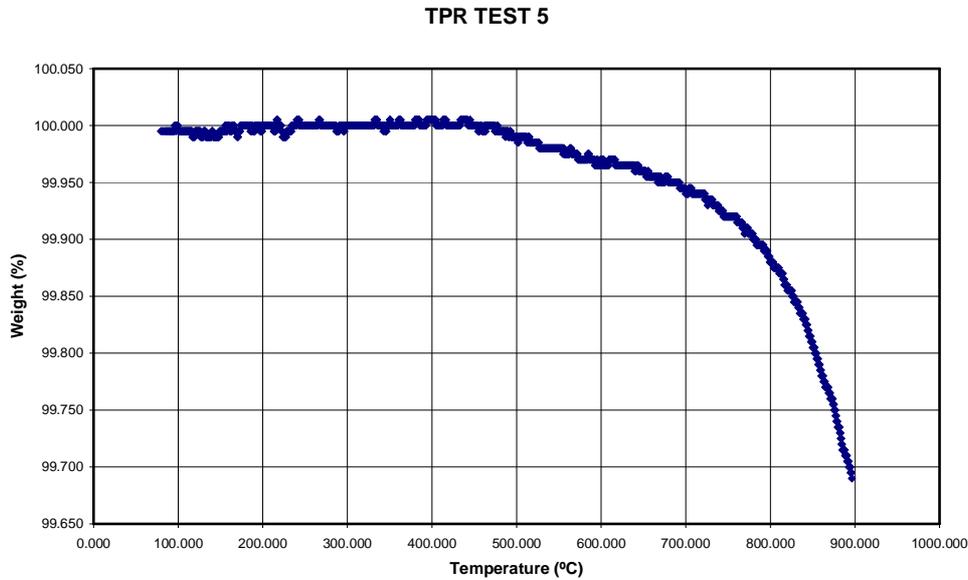


Figure 4.14. Weight% mass loss vs. Temperature at 25C/min.

We have seen that minimizing the scanning rate the reduction starts before and goes quickly, so we like to minimize, this scanning rate value.

### **TEST 6**

Now, the scanning rate has been decreased to 4K/min, the initial temperature is 500°C, because we know that the maximum rate of reduction goes from 500 to 900°C.

Bear in mind that the initial weight should be taken at 500°C, both without and with sample; it means that the sample should be initially heated to 500°C, weighted and initialized at zero and then starts the reduction session.

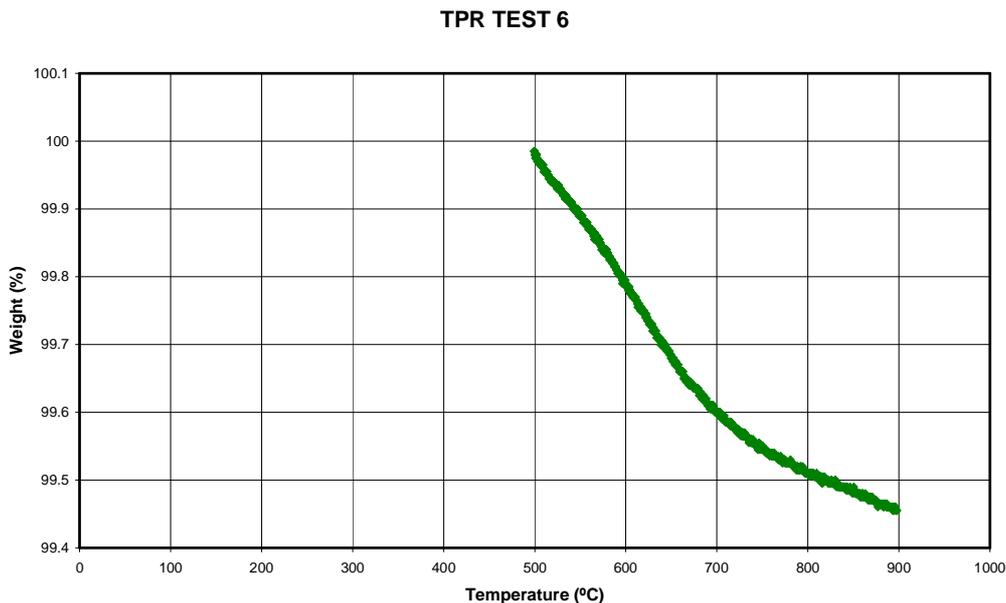


Figure 4.15. Weight% mass loss vs. Temperature at 4C/min, from 500°C up to 900°C.

## 5. DISCUSSION AND RESULTS

### 5.1 Experimental Results

In order to know if our results are within the range of the expected values and to determine if the results are good enough, a first analysis of the mass balance is done, based on the stoichiometric reaction. Using the different factors and conditions for the reaction, its mass balance is calculated, and then compared with the experimental results.

The complete reaction is:



Considering all the molecular weights:

$$\text{FeTiO}_3 = 55.85 + 47.87 + 48 = 151.45\text{g/mol}$$

$$\text{H}_2 = 2\text{g/mol}$$

$$\text{Fe} = 55.85\text{g/mol}$$

$$\text{TiO}_2 = 47.87 + 32 = 79.87\text{g/mol}$$

$$\text{H}_2\text{O} = 18\text{g/mol}$$

Assuming a flux of 100% Hydrogen during the reaction, the reduction will be as follows:

$$151.45 + 2 \rightarrow 55.85 + 79.87 + 18$$

$$153.45\text{g/mol} \rightarrow 135.72\text{ g/mol}$$

The weight lost is 17.73 g/mol, which is 11.5347% of mass loss during a complete reaction. In this analysis, a maximum reduction of ilmenite is considered, if not the 18g/mol assigned to the water molar mass would be lower. Bear in mind that there is equilibrium during the whole reaction in order to have a maximum and a total reduction.

In all tests, the sample was reduced with hydrogen/argon flux, 1/20 volume ratio instead of using a hundred per cent concentration of Hydrogen. It is not possible to have this maximum concentration of Hydrogen due to security measures, because hydrogen is very inflammable and a potential explosive; actually it is only feasible to find on terrestrial laboratories a maximum hydrogen concentration of 20/100 volume ratio.

See how the hydrogen concentration on the reduction affects on the next figure:

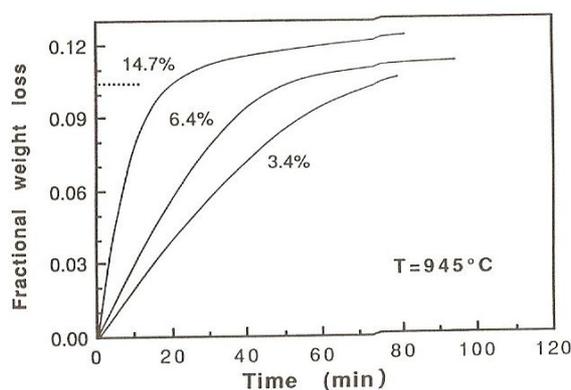


Figure 5.1. Different reduction at different hydrogen concentration during a TPR up to 945°C. [Zhao and Shadman]

Assuming this hydrogen volume ratio:

$$\text{With } 5\% \text{ H}_2 \text{ should be } 11.5347/20 = 0.5767\%$$

This value of 0.5767% of mass loss would be the maximum reduction for a flow of 1/20, Hydrogen/Argon, considering that all the Ilmenite is reduced.

Bearing in mind this value, now the same analysis should be compared with the experimental results (table 5.1).

#### Experimental Conditions:

| TEST Number  | Range of temperatures | Heating Rate (°C/min) | Flow H <sub>2</sub> /Ar | Initial Mass (mg) | Reduction (%) | Mass loss (g) | Molar weight (moles) |
|--------------|-----------------------|-----------------------|-------------------------|-------------------|---------------|---------------|----------------------|
| TEST 3       | 100-900°              | 10                    | 1/20                    | 67.51878          | 0.775         | 0.5233        | 0.0290               |
| TEST 5       | 100-900°              | 25                    | 1/20                    | 65.893            | 0.305         | 0.2009        | 0.0111               |
| TEST 6       | 500-900°              | 4                     | 1/20                    | 68,69154          | 0.545         | 0.3744        | 0.0208               |
| Ref. Value   |                       |                       | 1/20                    |                   | <b>0.5767</b> |               |                      |
| Ref. Value 2 |                       |                       | 100% H <sub>2</sub>     |                   | 11.5347       |               |                      |

Table 5.1. Experimental and reference values calculated from the experimental TPR data.

The closest value to the reference one has been Test 6, heated at a 4C/min as scan rate, however the highest reduction appeared at Test 3 with a scan rate of 10C/min. The highest scan rate in Test 5, which was heating at 25C/min was the lowest reduction results, lower than the reference value.

Test 3 resulted on a higher value than the reference one, which was supposed to be the maximum possible to be reduced due its perfect conditions. One possible explanation for this is that samples were not synthesized minerals, so there were contaminated. These external particles can have two possible effects on the reaction: slow the kinetics, or even can have the contrary effect. In this case there are two

possibly hypothesis to explain why the mass loss is higher than the one calculated as the reference value.

The first hypothesis is that the main contaminant of the sample which is the Magnetite ( $\text{Fe}_3\text{O}_4$ ) is probably also reduced, therefore the mass lost is higher.

However, a second hypothesis could be that the sample during its rapid cool down after the dry pre-process has gain some weight of Nitrogen Gas that is released when heating at this rate.

At high speed heating, the reaction can loose its equilibrium and for this reason the reduction is lower than expected, which happens in Test 5.

Test 6 has a small difference on the initial conditions; this is that the scanning rate was so slow that the initial temperature should be  $500^\circ\text{C}$  instead of  $100^\circ\text{C}$ . This can cause some changes on the final reduction results, however it also can be appreciated that the result is very close to the reference value, which means this scanning rate is also adequate.

Comparing three graphs (figure 5.2) is easy to realize that different scanning rate make changes not only on the final weight reduced but also in other parameters, like the initial reduction temperature, the velocity of reduction, and even the general behavior. In addition, a small difference on the temperature at which the reduction starts can be appreciated.

Test 5 and 3 follows a similar behavior, both start quite linear until temperatures around  $600^\circ\text{C}$ , then a great and quick decrease is experimented, and the slope has an increasing tendency when arriving to higher temperatures.

In table 5.2, the tendency lines that the curves at different tests follow, are shown. As you may notice the higher the slope is, which means that it is decreasing faster; except for the scan rate  $4\text{C}/\text{min}$ , when the faster decrease is appreciated to be around  $700^\circ\text{C}$ .

| Scan Rate | Temperature Range | Tendency Line (Slope)         |
|-----------|-------------------|-------------------------------|
| 25 C/min  | 500-600           | $y = -0.0002x + 100.11$       |
|           | 600-700           | $y = -0.0003x + 100.12$       |
|           | 700-800           | $y = -0.0006x + 100.37$       |
|           | 800-900           | $y = -0.002x + 101.51$        |
| 10 C/mim  | 500-600           | $y = -6\text{E}-05x + 100.04$ |
|           | 600-700           | $y = -0.0004x + 100.25$       |
|           | 700-800           | $y = -0.0019x + 101.29$       |
|           | 800-900           | $y = -0.0056x + 104.28$       |
| 4 C/min   | 500-600           | $y = -0.0018x + 100.9$        |
|           | 600-700           | $y = -0.0019x + 100.94$       |
|           | 700-800           | $y = -0.0009x + 100.21$       |
|           | 800-900           | $y = -0.0006x + 99.964$       |

Table 5.2. Tendency lines of the TPR curves.

Test 3, remember it has 10C/min as scan rate, starts slightly later than Test 5. You can notice that Test 5 starts around 500°C, while Test 3 starts to decrease around 625°C. However, the slope and velocity of reduction for a high scan rate (25C/min) can be translated into a slow velocity of reduction and lower slope.

Now, comparing Test 6 with Test 5 and 3, it is very easy to distinguish a very different behavior. While 5 and 3 are following a smooth and convex curve decrease, Test 6 starts to decrease at higher velocity; greater slope appears to happen between temperatures 500 and 700°C, then it becomes slower until 900°C.

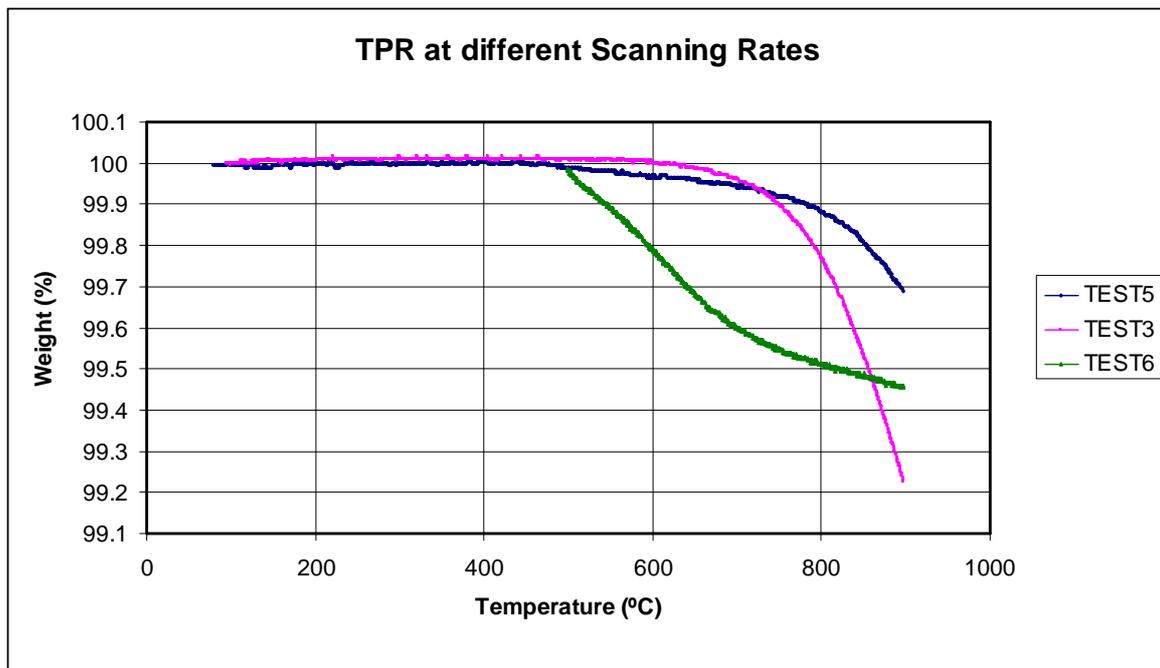


Figure 5.2. Weight% mass loss vs. Temperature at three different scan rates: TEST5 (25C/min), TEST 3 (10C/min) and TEST 6 (4C/min)

During the experiments, an unexpected phenomenon was observed during the drying test of the samples process. All samples were heated with gas Nitrogen from 100 to 900°C, as explained before, to make sure water and humidity and other contaminants such as carbon is evaporated and not interferes in the ilmenite reduction. In any case, the sample gained weight at the end of the heating.

In figure 5.3 you can appreciate this increase, in Test 2 is higher than in Test 4, probably due to the humidity of the environment. There is a clear loss of weight until 500°C; where the maximum loss is experimented, probably all the water and other small traces are evaporated at this temperature and released. However, the curve change its behavior completely following an increasing tendency after that.

There can be some hypothesis to be done due to this phenomenon. The most appropriate one could be that Nitrogen reacts somehow with Ilmenite. Probably at high temperatures, the molecules are vibrating so strong that some Nitrogen atoms can enter between the interstices that the vibrations leave between the atoms and stay there, increasing the weight of the sample. These molecules are known to be

evaporated again during the cool down that is done before the reduction with hydrogen starts again. However, this cool down can be produced at too high speed and some of these Nitrogen molecules can remain in the ilmenite and released during the reduction. This will mean that not all the ilmenite is reduced during our loss weight but also some gas nitrogen is released.

It is known that the terrestrial ilmenite is an important mantle reservoir. Its origin is not very well known, and it is only suggested that the nitrogen can replace oxygen in the crystal structure but not demonstrated (Madiba CCP, 1998).

There is not enough information and more detailed study about this should be done in order to confirm these hypotheses, which is beyond the scope of this project.

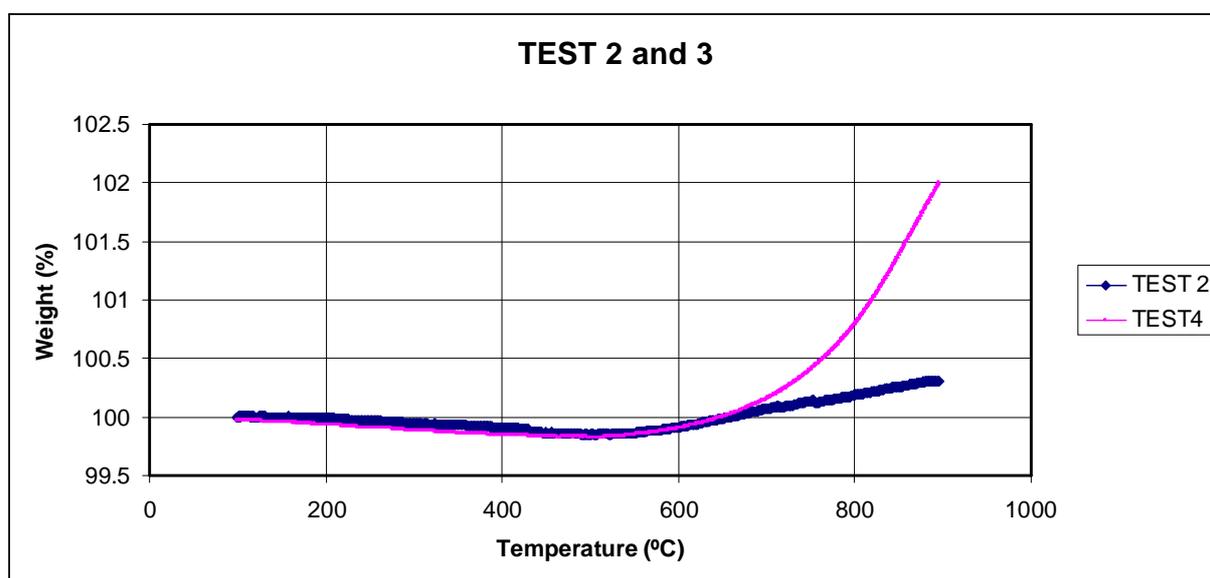


Figure 5.3. weight% loss of mass vs. Temperature during the preheat of the sample up to 900°C.

## 5.2. Conclusions and Final Work

Oxygen is a major element on the Moon, more than 40% of the total composition of the moon is Oxygen, and around 60 wt% is oxygen.

The main constraints for the utilization of this oxygen are the form that it is found on the lunar regolith: embedded in other components and in ice water form; and consequently the high energy needed to extract it and convert it into gas form.

Forthcoming missions are thinking to go back to the Moon: NASA's Constellation Program is the most ambitious one. Setting up a lunar base will need improved ISRU capability. For a first human settlement on the moon, oxygen will be the first need to be supplied due to the lack of atmosphere in our satellite. According to some life support analysis and data from Apollo missions and International Space Station, humans need a mean value of gas oxygen close to 1kg per day.

More than 20 methods have been proposed by some scientist to obtain oxygen from the surface of the moon, using in situ resources. The most feasible one seems to be the Ilmenite reduction with Hydrogen because there is huge quantities of this mineral on the moon, specially on the Hi-Ti mares and mare rocks, the technology to be developed is not as much as the one already developed, as far as it is only a three steps reaction the probabilities of failure decrease and the probability of low mass and reliable system increase.

It is needed a considerable energy to do the reaction but not as high as other processes; and the most positive aspect is that hydrogen is recycled. Kynetics are fast and the reaction is not too sensible to the change of temperature.

Hydrogen is known to be in the Lunar regolith. Its origin is from the Solar Wind, from meteorites and asteroids impacts and also in the shadowed areas, mostly concentrated in ice water form in the lunar poles. Neutron Spectrometers and other equipments carried by missions from most of the Space Agencies in the world revealed that there are important deposits of hydrogen in the Moon. It is estimated that there is around some billions metric tones of hydrogen on the moon. Factors such as regolith particle size, inclination of the moon with respect to the ecliptic, geological profile of the lunar surface, the low temperatures when shadow or night, the maturity of the soil, the neutron spectrometer and other equipments collected data, the known depth of the hydrogen concentration, are the ones important for a good estimation of the hydrogen quantity.

Ilmenite in the moon is very abundant, it was found in the Apollo samples, especially in the Apollo11 and Apollo 17 which were from the ilmenite-rich mare basalts; in this samples it was about 25 percent of available ilmenite. In mare soils it is around 9 percent, and the hi-Ti mare soils can concentrate 5-10 percent of the soil as 90 percent pure ilmenite.

As ilmenite may be rich in solar-wind derived hydrogen, it could contain as much as 1000-2000ppm hydrogen in the fine-grained ilmenite, which will be an extra positive point. The hydrogen embedded in the ilmenite will be also released during the reduction, increasing the efficiency of the reaction.

Extracting solar wind and meteorites implanted hydrogen requires heating soil to about 700°C and at this point only around the 10% of the gas is recovered. In contrast, icy regolith heated to about 100°C gives off water as an easily collected and stored gas. Per unit mass, it takes roughly two orders of magnitude less energy to extract hydrogen from icy polar regolith than it does by roasting soil at the equator.

There could be an obvious issue for this project: why do we need to extract oxygen from the regolith if it is known that there is water on the moon, and that melting this water ice and electrolyzing it is the easiest way to get it? A simple answer can be that the ice is known to be only at the poles, which have lot of inconvenience for human life; long days and nights with high gradients of temperature, shadow and light times which means energy constraints, as well as an added convenient for the mission analysis because going to the poles is not as easy as going to the midlatitudes. In addition, as you may have known, if the Moon is thought to be a future launch facility, the close to the equator, the best for the launching area.

TPR experiments were successful and revealed a high efficiency of the reaction. Although it could seem that the amount of water released is not high, considering the hydrogen concentration in the flow, this quantity is appropriate and even improved. A maximum ideal reduction weight loss would be 11.5347% in a 100% hydrogen flux. However, the laboratory flux of hydrogen was only a 5% concentration, which can be translated as a reduction also in the maximum possible weight loss in 0.5767%.

High scanning rates (25C/min) affect the equilibrium of the reaction and therefore the efficiency. Scan rates around 10C/min seems to be the most desirables, the efficiency is increased up to 0.775, this can suggest that maybe part of the contamination elements such as magnetite are also reduced during the process, releasing water vapor. However, a too low scan rate (4C/min) shows better reaction kinetics, but the maximum quantity reduced is not the as high as at 10C/min.

The starting reduction temperature seems to be close to 500°C. It slightly varies from each scan rate. At 25C/min in Test 5 it seems to start to reduce at lower temperatures, closer to 400°C. This decrease on the initial reduction temperature can be very interesting; it can be analyzed at nanoscale in order to be able to understand better this starting point, this knowledge could end up in studies able to reduce the energy needed for the reaction.

Ilmenite seems to be reactive to Nitrogen, this phenomenon is not very well understood, however it has been demonstrated that the ilmenite present in the Earth mantle has a high concentration of Nitrogen. It is known that the nitrogen is not located in liquid inclusions and its origin is uncertain. It is suggested that N<sub>2</sub> must replace oxygen in the crystal structure, but it is not demonstrated. (Madiba CCP, 1998)

### 5.3. Future work

Some future work is recommended to increase the amount of data in order to have a more complete analysis and go further, especially to have more factors to compare and to improve the chemical reduction of the Ilmenite. Most of this future work suggestions are related to improvements on the experimental part.

Pre-heat the sample with Argon instead of Nitrogen. This can solve the unexpected phenomenon of the increased in weight or can give a better explanation.

Test different ilmenite samples with a variety of particle size, to see if this factor can change the reduction result in a remarkable manner.

Test more scanning rates values such as 4C/min but starting from 100°C instead of 500°C and more values between 5 and 15C/min. During the progress of our project this could not be performed due to time constrains and availability of the equipment.

It would be interesting to add some elements, such as Cobalt to the hydrogen, or adding Iron or doing a preoxidation to the ilmenite before the TPR. Kinetics and efficiency are known to be improved.

It is highly recommended to do the reduction at higher temperatures, for example up to 1200°C, to see how the reduction rate is slowed down and when it is stopped. Also it will be great to examine the range of 400 to 650°C at very low scan rate, because it seems to be where the first reductions at nanoscale are starting to appear.

A better estimation of the hydrogen quantity and ilmenite reserves can be achieved, bearing in mind the updated and recent data obtained during the last missions to the moon or lunar orbit. These data is currently under investigation and I am sure that will give us very interesting and relevant scientific data.

The higher recommendation for future work would be to do the experiments with some Apollo lunar samples. Although it is very difficult to get one and the terrestrial analogs are good enough for first steps, it will not be as accurate as using lunar material, with a specific particle size and composition. In addition, the possibility of doing the experiment in situ, this is in the surface on the moon will be also a positive point: how gravity, absence of atmosphere, temperatures and landing site can affect the final product.

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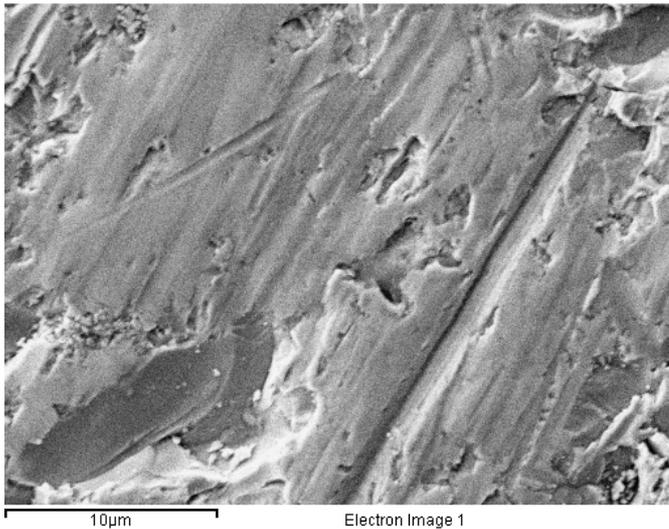
## **7. ANNEXES**

## ANNEX A - SEM Characterization

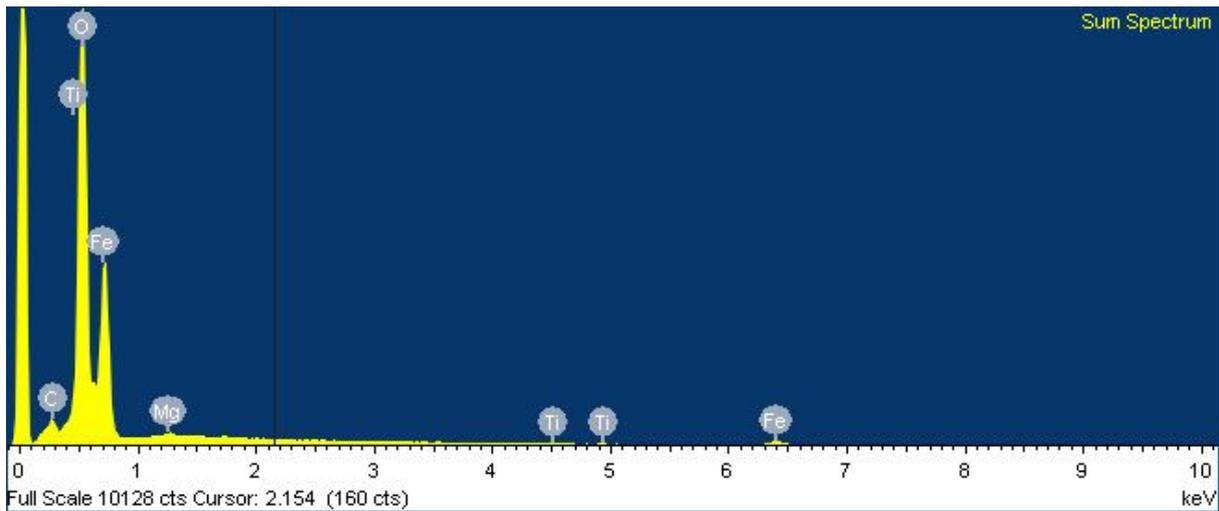
Again, after placing the sample holder inside the SEM, with a working distance (WD) of 7.3mm and at 8kv some images and quantified data was extracted.

### Sample 1

**Point 1.** Sample 1, first point analyzed:

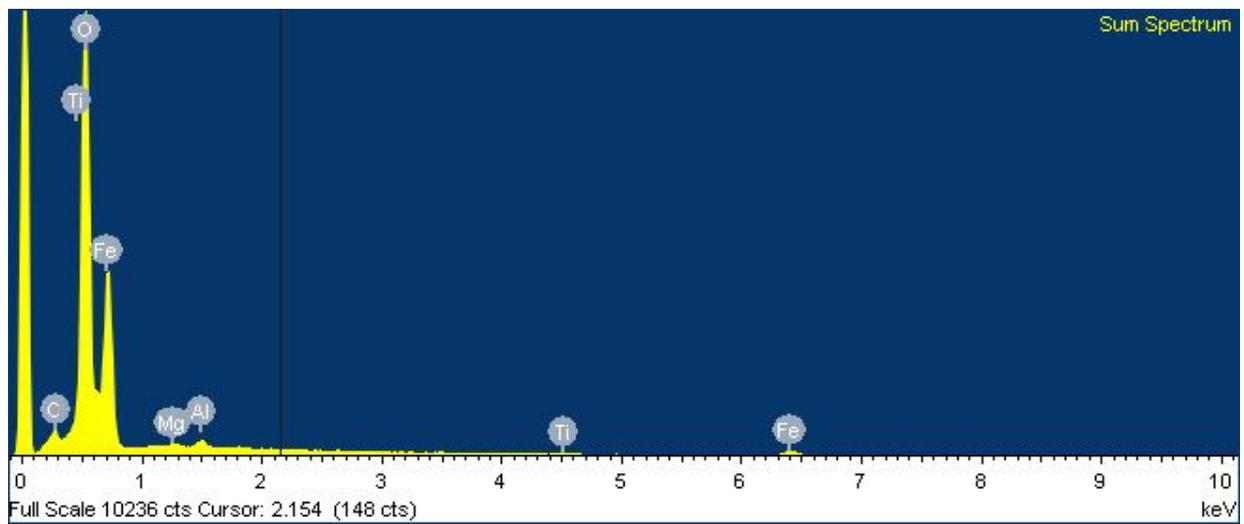
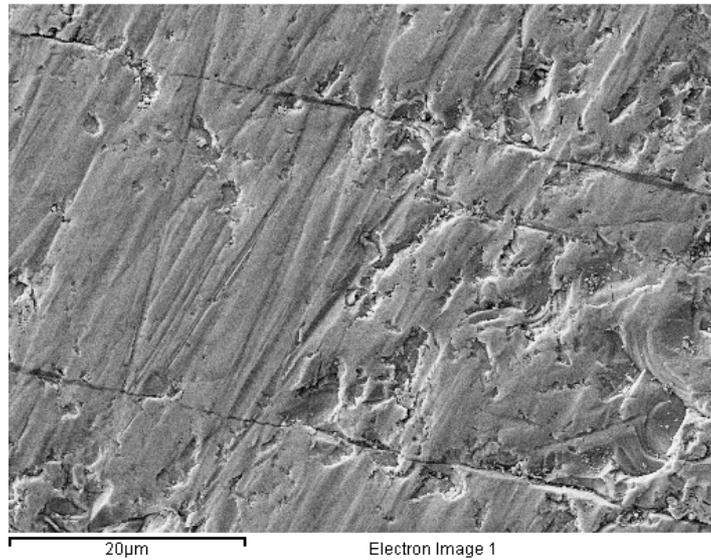


|            |         |
|------------|---------|
| <b>Mag</b> | 9.53K x |
| <b>WD</b>  | 7.3mm   |
| <b>EHT</b> | 0.00kV  |



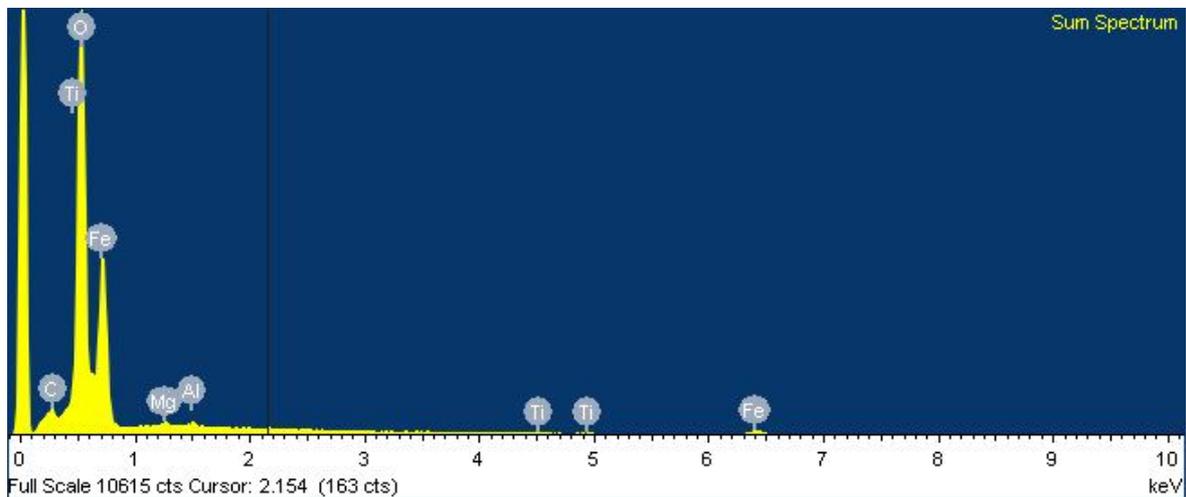
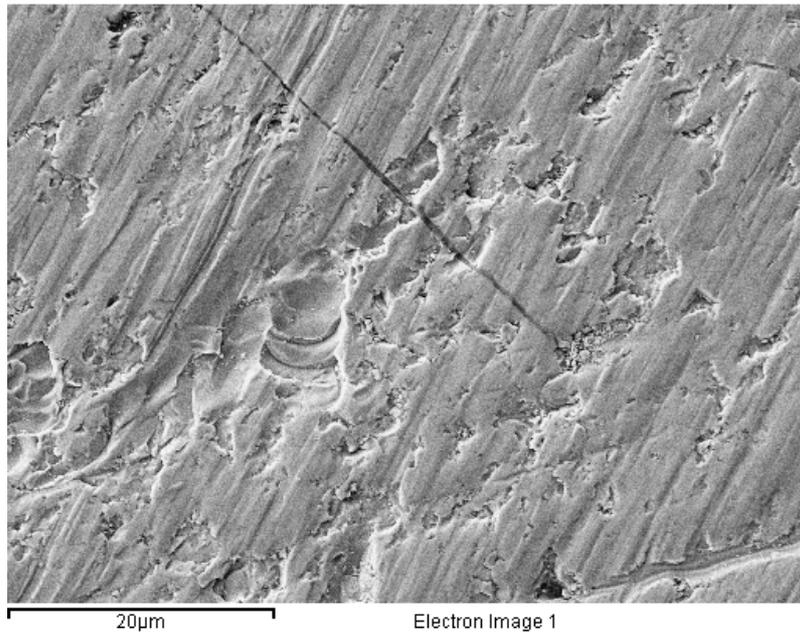
| Element | App<br>Conc. | Intensity<br>Corrn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|---------------------|--------------|------------------|---------|
| C K     | 0.05         | 1.2438              | 0.96         | 0.10             | 2.49    |
| O K     | 2.44         | 2.1020              | <b>29.58</b> | 0.73             | 57.48   |
| Mg K    | 0.01         | 1.0756              | 0.19         | 0.04             | 0.24    |
| Ti L    | 0.41         | 0.7811              | <b>13.33</b> | 1.96             | 8.65    |
| Fe L    | 1.44         | 0.6514              | <b>55.93</b> | 1.32             | 31.13   |
| Totals  |              |                     | 100.00       |                  |         |

## Point 2 (S1)



| Element | App<br>Conc. | Intensity<br>Corrn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|---------------------|--------------|------------------|---------|
| C K     | 0.04         | 1.2333              | 0.88         | 0.10             | 2.29    |
| O K     | 2.52         | 2.1239              | <b>29.44</b> | 0.74             | 57.29   |
| Mg K    | 0.01         | 1.0757              | 0.23         | 0.04             | 0.29    |
| Al K    | 0.02         | 1.1082              | 0.39         | 0.05             | 0.45    |
| Ti L    | 0.40         | 0.7784              | <b>12.67</b> | 2.02             | 8.23    |
| Fe L    | 1.49         | 0.6563              | <b>56.39</b> | 1.36             | 31.44   |
| Totals  |              |                     | 100.00       |                  |         |

### Point 3 (S1)

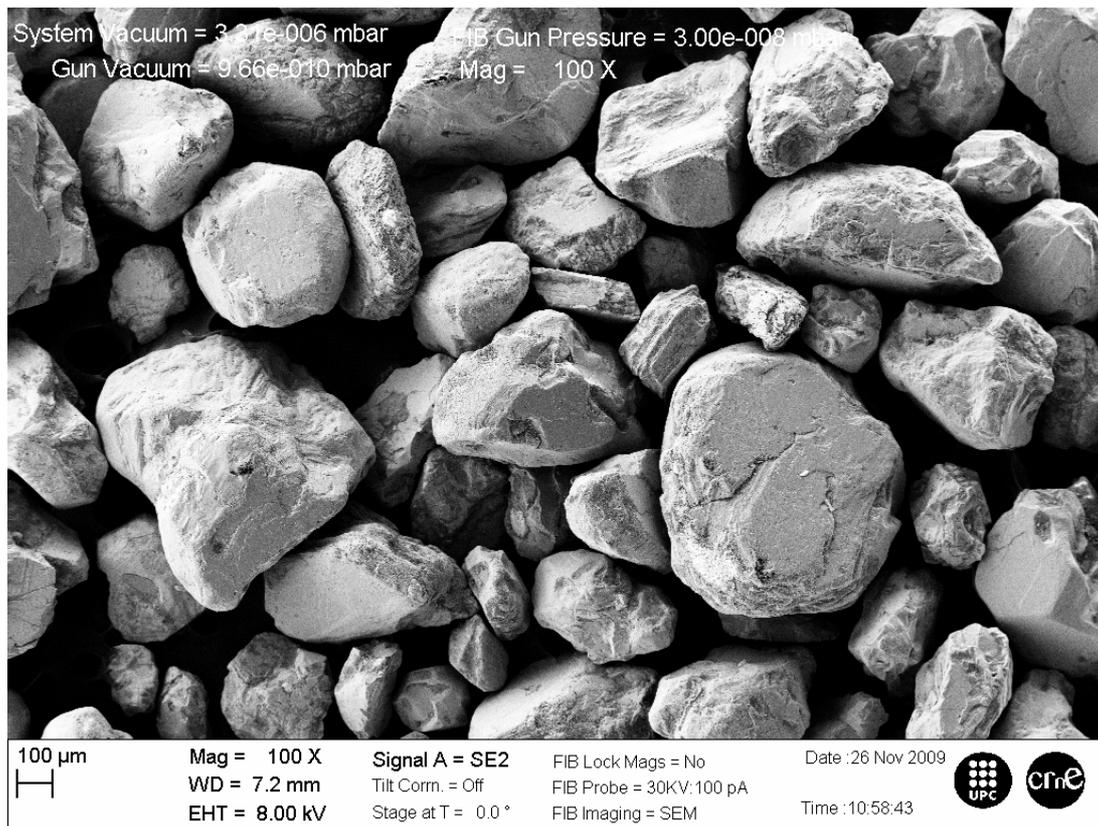


| Element | App<br>Conc. | Intensity<br>Corn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|--------------------|--------------|------------------|---------|
| C K     | 0.04         | 1.2449             | 0.79         | 0.10             | 2.06    |
| O K     | 2.56         | 2.0606             | <b>29.30</b> | 0.71             | 57.22   |
| Mg K    | 0.01         | 1.0782             | 0.20         | 0.04             | 0.26    |
| Al K    | 0.01         | 1.1104             | 0.19         | 0.04             | 0.22    |
| Ti L    | 0.48         | 0.7850             | <b>14.53</b> | 1.92             | 9.47    |
| Fe L    | 1.51         | 0.6459             | <b>55.00</b> | 1.29             | 30.77   |
| Totals  |              |                    | 100.00       |                  |         |

This area seems to be more pure, at 5000 iterations the program only could detect Fe, Ti and O.

## SAMPLE 2

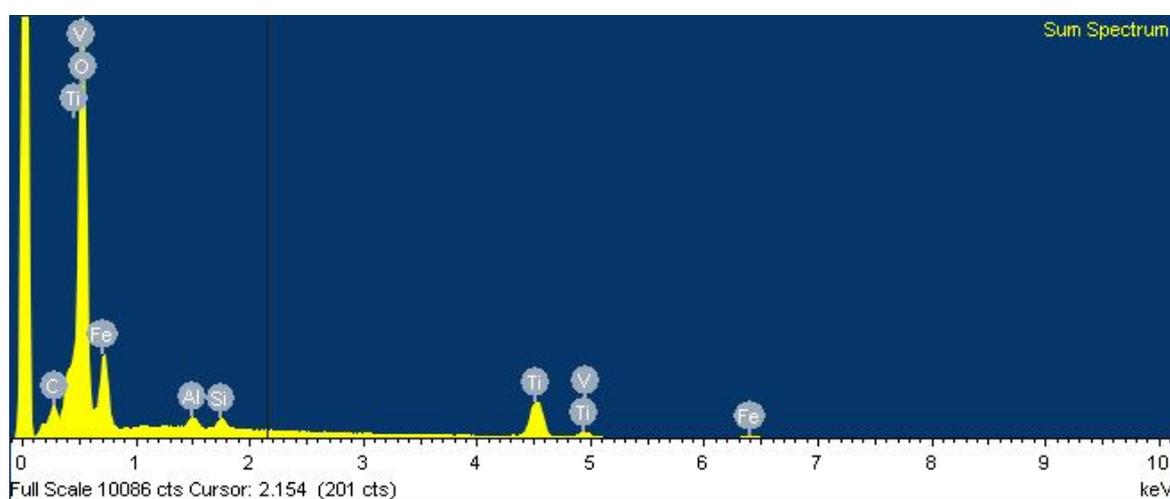
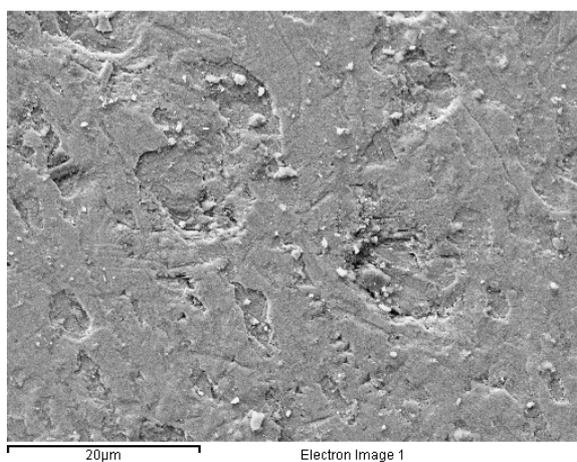
### General View



|            |        |
|------------|--------|
| <b>Mag</b> | 100 x  |
| <b>WD</b>  | 7.2mm  |
| <b>EHT</b> | 8.00kV |

Sample 2 is found in powder, grains from 300µm and bigger. Some of these grains have been pointed with the SEM, because it was seen that not all of them present the same structure and more probably its composition.

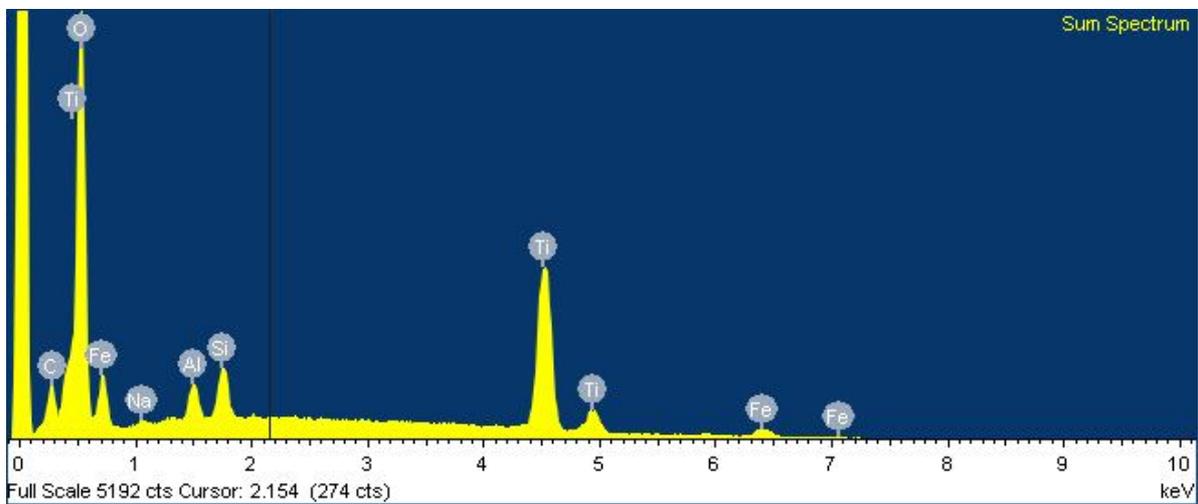
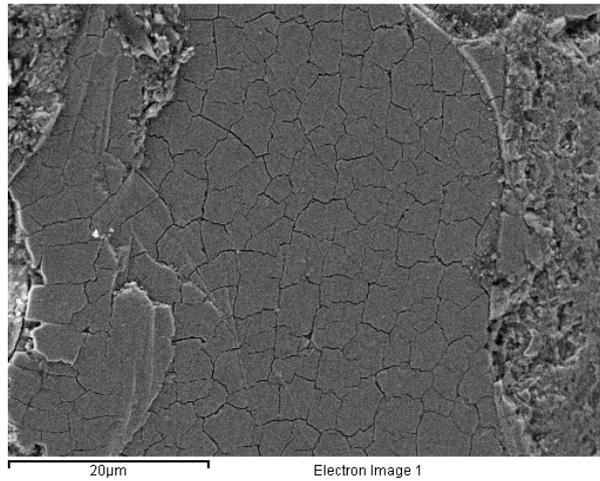
## Point 1 S2



| Element | App<br>Conc. | Intensity<br>Corrn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|---------------------|--------------|------------------|---------|
| C K     | 0.05         | 1.4139              | 0.73         | 0.07             | 1.85    |
| O K     | 1.75         | 1.2033              | <b>29.81</b> | 1.03             | 56.21   |
| Al K    | 0.02         | 1.1593              | 0.42         | 0.03             | 0.47    |
| Si K    | 0.02         | 1.1676              | 0.41         | 0.04             | 0.44    |
| Ti L    | 1.61         | 0.8612              | <b>38.09</b> | 1.57             | 23.99   |
| V L     | 0.24         | 0.4756              | 10.49        | 2.58             | 6.21    |
| Fe L    | 0.47         | 0.4789              | <b>20.05</b> | 0.78             | 10.83   |
| Totals  |              |                     | 100.00       |                  |         |

Titanium and Fe appear so quickly from the beginning of the iteration.

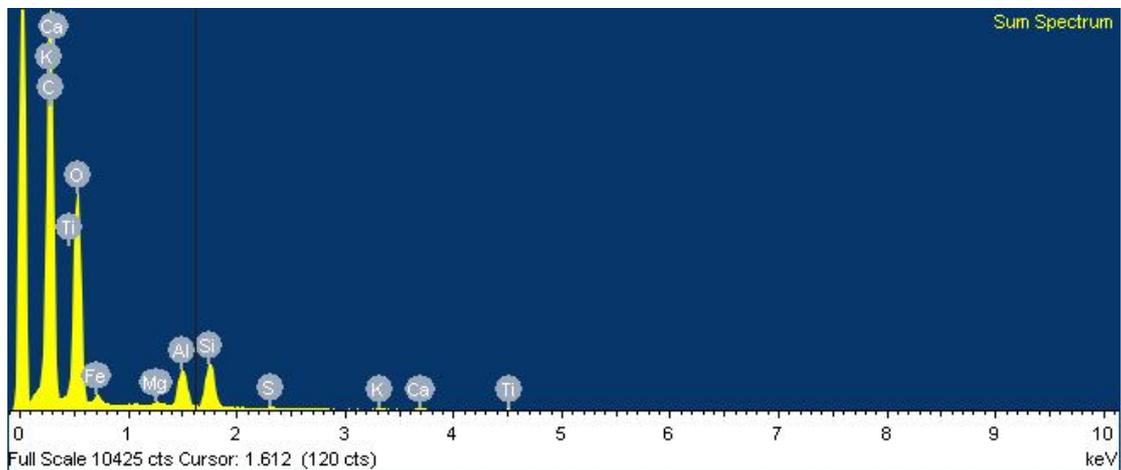
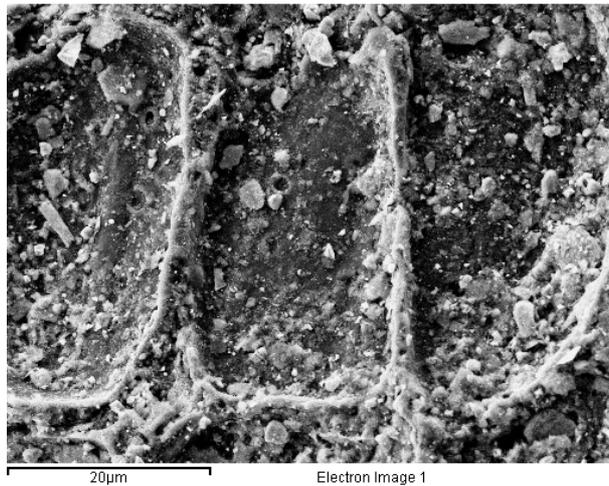
## Point 2 (S2)



| Element | App<br>Conc. | Intensity<br>Corrn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|---------------------|--------------|------------------|---------|
| C K     | 0.02         | 1.3531              | 2.21         | 0.15             | 5.04    |
| O K     | 0.33         | 1.2790              | <b>33.88</b> | 1.15             | 57.92   |
| Na K    | 0.00         | 1.4488              | 0.23         | 0.06             | 0.28    |
| Al K    | 0.01         | 1.1543              | 1.59         | 0.09             | 1.62    |
| Si K    | 0.02         | 1.1508              | 2.70         | 0.13             | 2.63    |
| Ti L    | 0.26         | 0.8145              | <b>42.26</b> | 1.89             | 24.14   |
| Fe L    | 0.06         | 0.4805              | <b>17.12</b> | 0.81             | 8.39    |
| Totals  |              |                     | 100.00       |                  |         |

Titanium appear easily and having a high peak in Kalpha energy. Iterations finished at 5000 because there were no great changes and the emission was very low.

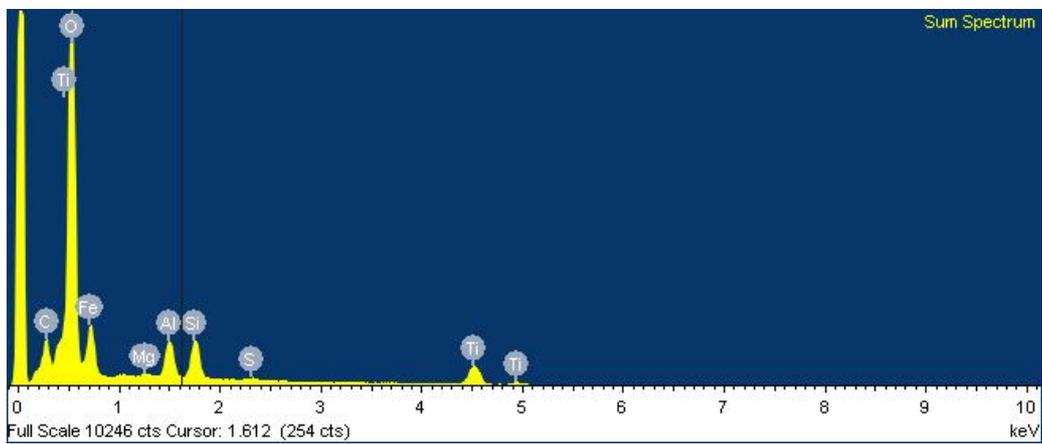
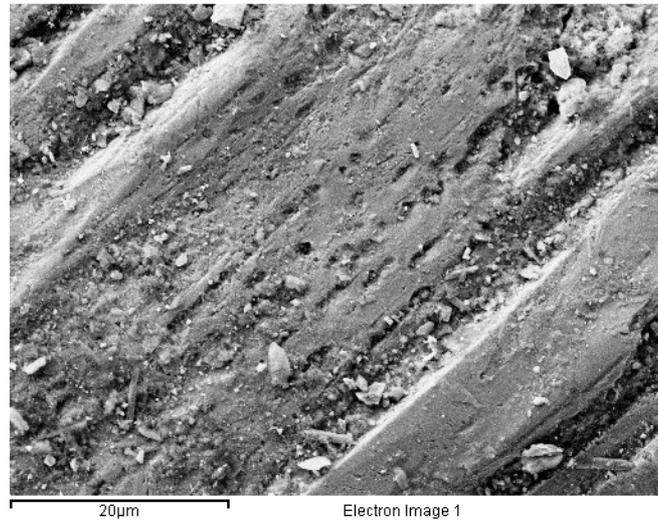
### Point 3 (S2)



| Element | App<br>Conc. | Intensity<br>Corrn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|---------------------|--------------|------------------|---------|
| C K     | 2.30         | 1.4655              | 37.46        | 3.20             | 54.58   |
| O K     | 1.47         | 1.2168              | <b>28.82</b> | 2.46             | 31.53   |
| Mg K    | 0.01         | 1.1590              | 0.16         | 0.04             | 0.12    |
| Al K    | 0.12         | 1.1231              | 2.52         | 0.22             | 1.63    |
| Si K    | 0.17         | 1.0888              | 3.63         | 0.32             | 2.26    |
| S K     | 0.01         | 1.0196              | 0.23         | 0.05             | 0.13    |
| K K     | 0.01         | 1.0549              | 0.33         | 0.07             | 0.15    |
| Ca K    | 0.02         | 0.9796              | 0.43         | 0.08             | 0.19    |
| Ti L    | 0.37         | 0.4110              | <b>21.80</b> | 6.64             | 7.96    |
| Fe L    | 0.10         | 0.4931              | <b>4.62</b>  | 0.55             | 1.45    |
| Totals  |              |                     | 100.00       |                  |         |

This is a very different structured grain, it has a very clear pattern, regular cells on the surface. It has a lot of Carbon, seems to be a completely different mineral.

## Point 4 (S2)



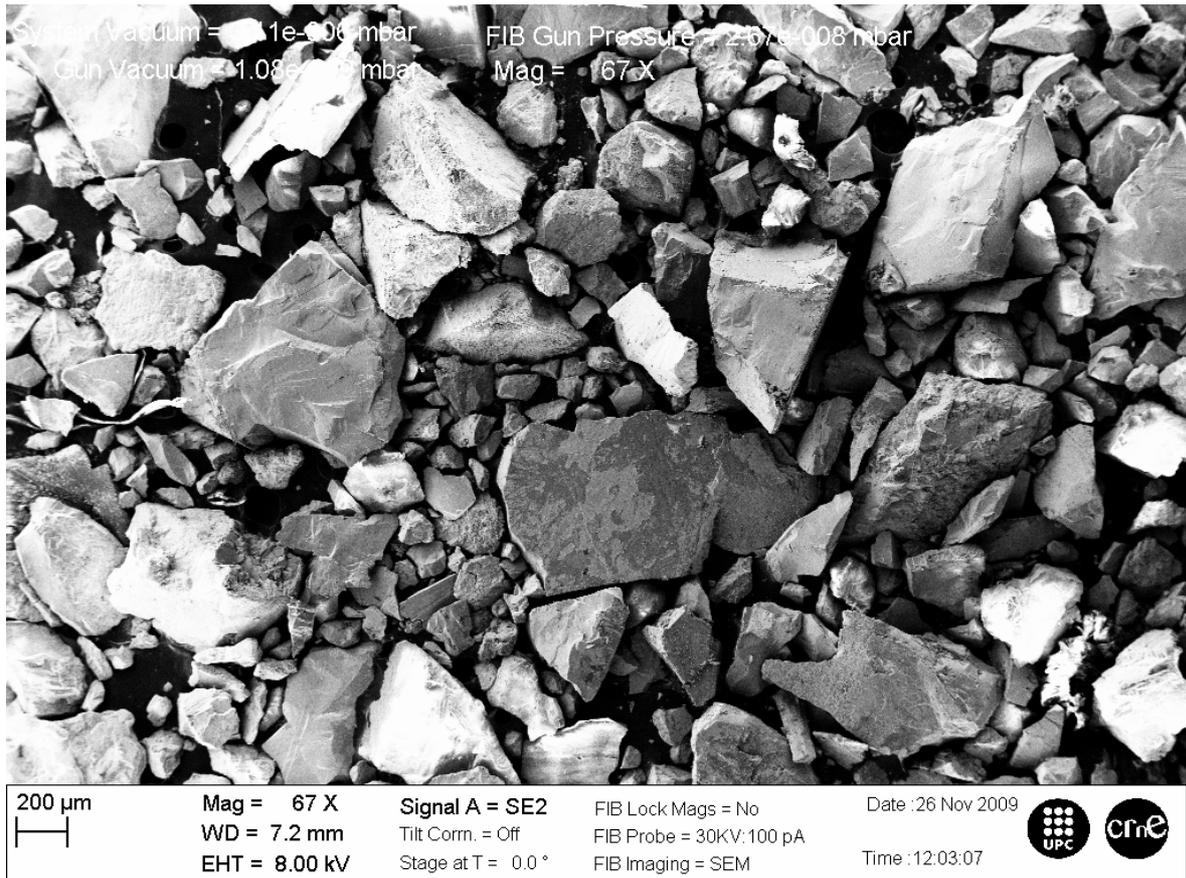
| Element | App<br>Conc. | Intensity<br>Corrn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|---------------------|--------------|------------------|---------|
| C K     | 0.12         | 1.2997              | 2.27         | 0.12             | 5.00    |
| O K     | 2.09         | 1.4206              | <b>36.80</b> | 0.95             | 60.91   |
| Mg K    | 0.01         | 1.1384              | 0.12         | 0.04             | 0.13    |
| Al K    | 0.10         | 1.1431              | 2.11         | 0.08             | 2.07    |
| Si K    | 0.12         | 1.1383              | 2.62         | 0.09             | 2.47    |
| S K     | 0.01         | 1.0992              | 0.21         | 0.05             | 0.17    |
| Ti L    | 1.10         | 0.7901              | <b>34.94</b> | 1.62             | 19.32   |
| Fe L    | 0.42         | 0.5008              | <b>20.93</b> | 0.70             | 9.93    |
| Totals  |              |                     | 100.00       |                  |         |

Titanium appears very quickly, on the análisis, which can indicate that there is quite high quantity.

## SAMPLE 3

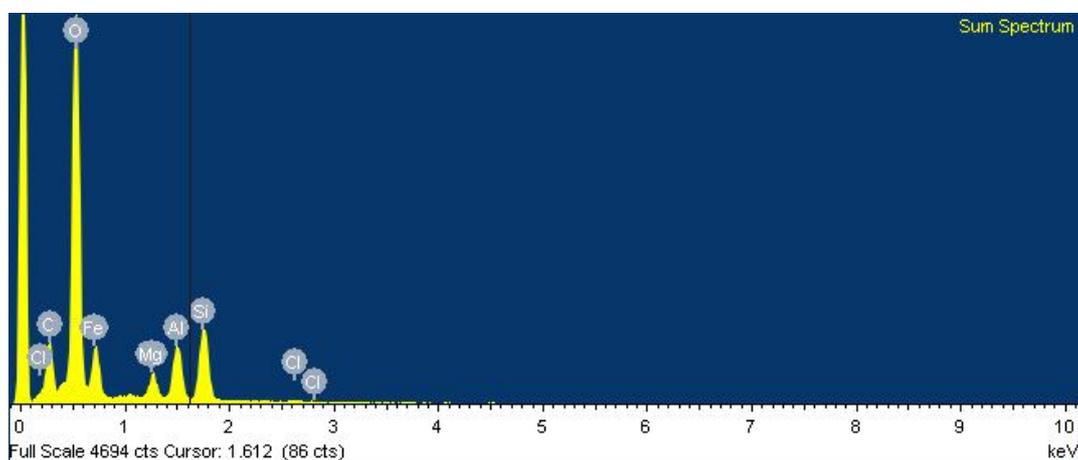
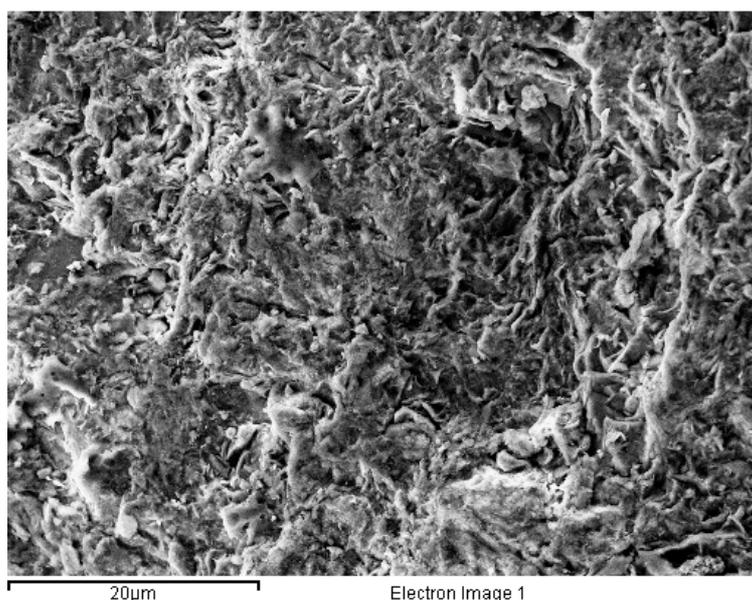
### General View

This is a general view of the sample 3, shape of grains are very different between them, they range from 100µm up to 500µm.



|            |        |
|------------|--------|
| <b>Mag</b> | 67 x   |
| <b>WD</b>  | 7.2mm  |
| <b>EHT</b> | 8.00kV |

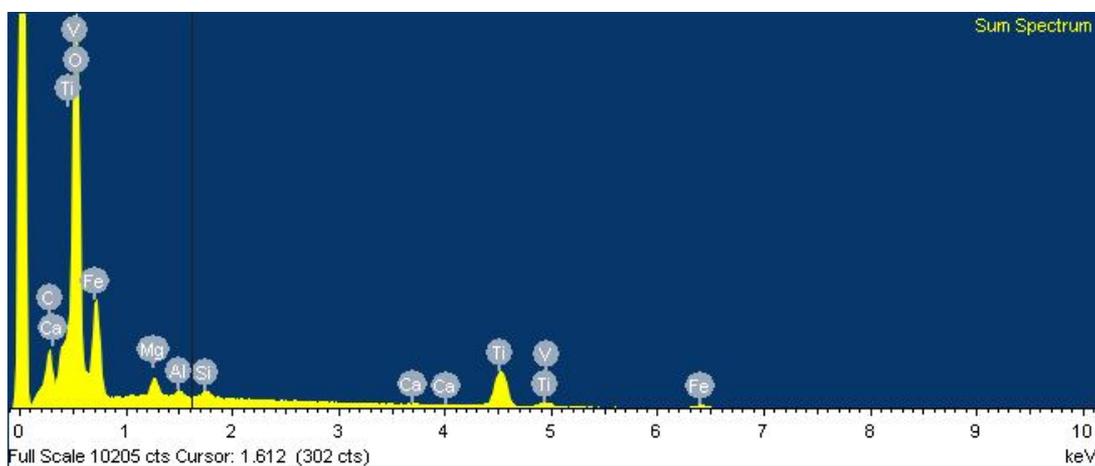
## Point 1 (S3)



| Element | App<br>Conc. | Intensity<br>Corn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|--------------------|--------------|------------------|---------|
| C K     | 0.30         | 1.0064             | 10.04        | 0.37             | 17.90   |
| O K     | 2.84         | 2.2066             | <b>42.62</b> | 0.61             | 57.03   |
| Mg K    | 0.08         | 1.1206             | 2.30         | 0.12             | 2.03    |
| Al K    | 0.18         | 1.1016             | 5.38         | 0.17             | 4.27    |
| Si K    | 0.30         | 1.0777             | 9.17         | 0.22             | 6.99    |
| Cl K    | 0.01         | 0.8715             | 0.47         | 0.13             | 0.28    |
| Fe L    | 0.55         | 0.6061             | <b>30.02</b> | 0.85             | 11.51   |
| Totals  |              |                    | 100.00       |                  |         |

No titanium in the composition, energy emission was very low, so iterations finished at 5000.

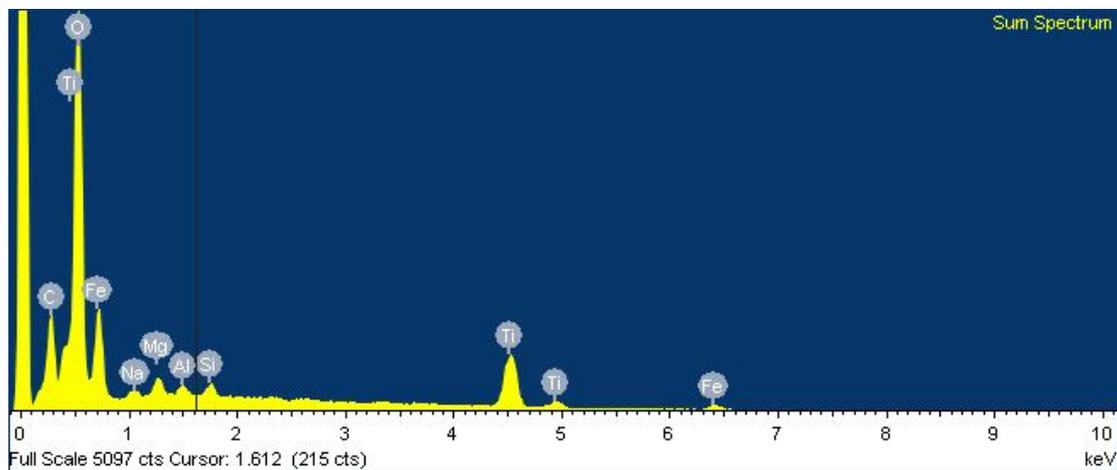
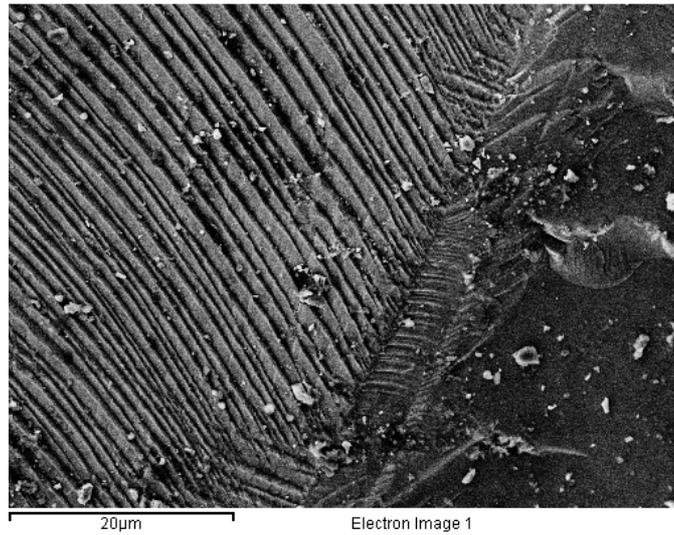
## Point 2 (S3)



| Element | App<br>Conc. | Intensity<br>Corrn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|---------------------|--------------|------------------|---------|
| C K     | 0.10         | 1.3944              | 1.66         | 0.09             | 4.26    |
| O K     | 1.42         | 1.2295              | <b>26.78</b> | 0.97             | 51.64   |
| Mg K    | 0.03         | 1.1416              | 0.65         | 0.04             | 0.83    |
| Al K    | 0.01         | 1.1555              | 0.20         | 0.03             | 0.23    |
| Si K    | 0.01         | 1.1674              | 0.26         | 0.03             | 0.29    |
| Ca K    | 0.01         | 1.1250              | 0.26         | 0.06             | 0.20    |
| Ti L    | 1.29         | 0.8312              | <b>35.64</b> | 1.79             | 22.96   |
| V L     | 0.20         | 0.4904              | 9.63         | 2.37             | 5.83    |
| Fe L    | 0.54         | 0.4959              | <b>24.91</b> | 0.95             | 13.76   |
| Totals  |              |                     | 100.00       |                  |         |

Titanium has appeared quickly from the beginning.

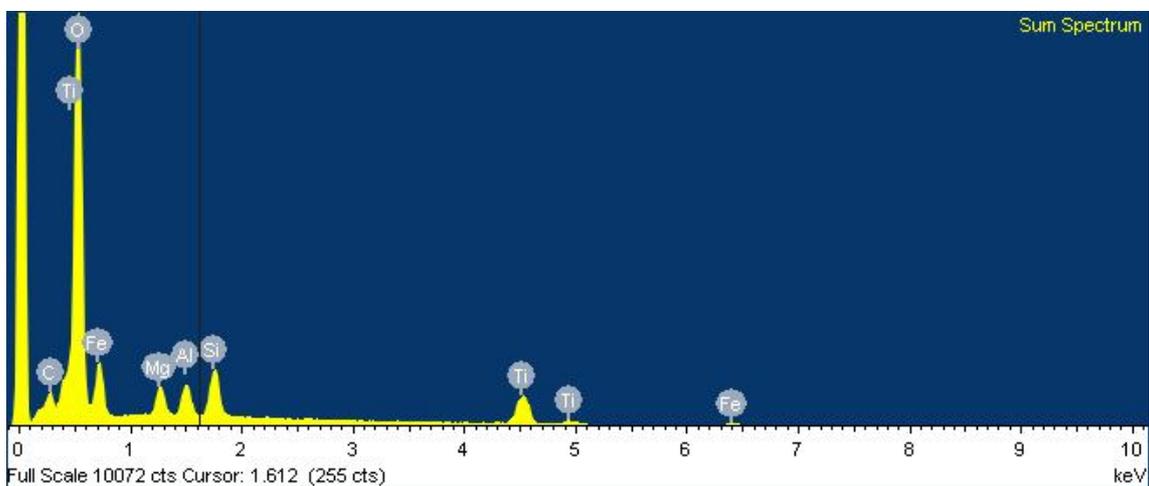
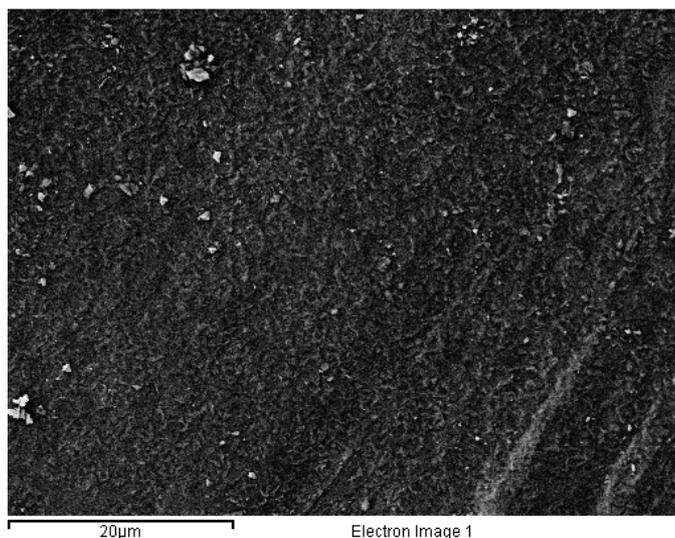
### Point 3 (S3)



| Element | App Conc. | Intensity Corn. | Weight%      | Weight% Sigma | Atomic% |
|---------|-----------|-----------------|--------------|---------------|---------|
| C K     | 0.13      | 1.3876          | 3.91         | 0.18          | 9.27    |
| O K     | 0.91      | 1.3413          | <b>29.37</b> | 0.95          | 52.23   |
| Na K    | 0.01      | 1.4175          | 0.26         | 0.05          | 0.32    |
| Mg K    | 0.02      | 1.1348          | 0.73         | 0.06          | 0.85    |
| Al K    | 0.01      | 1.1436          | 0.37         | 0.05          | 0.39    |
| Si K    | 0.02      | 1.1515          | 0.60         | 0.06          | 0.61    |
| Ti L    | 0.73      | 0.7960          | <b>39.40</b> | 1.86          | 23.41   |
| Fe L    | 0.30      | 0.5092          | <b>25.36</b> | 0.95          | 12.92   |
| Totals  |           |                 | 100.00       |               |         |

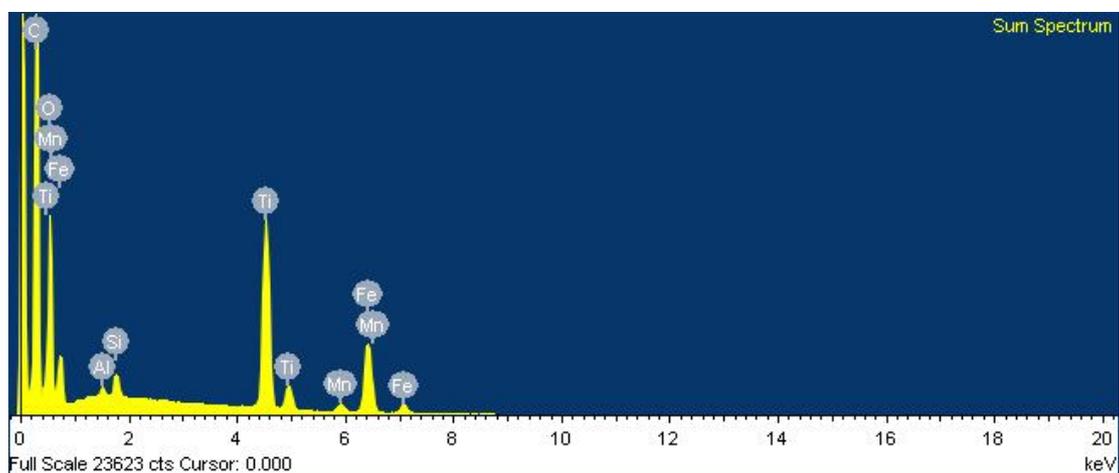
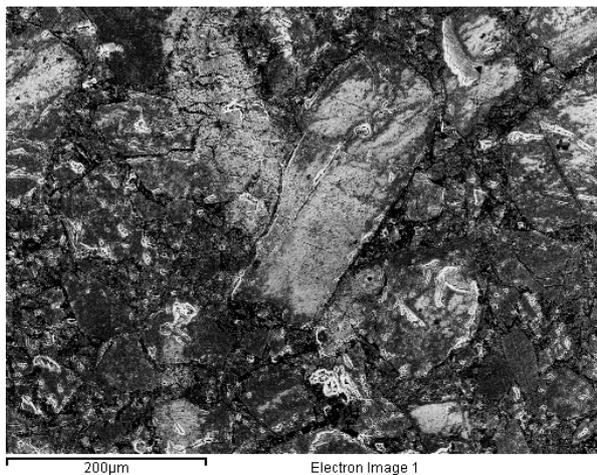
Ti, Fe and Oxygen have been easily and quickly detected.

## Point 4 (S3)

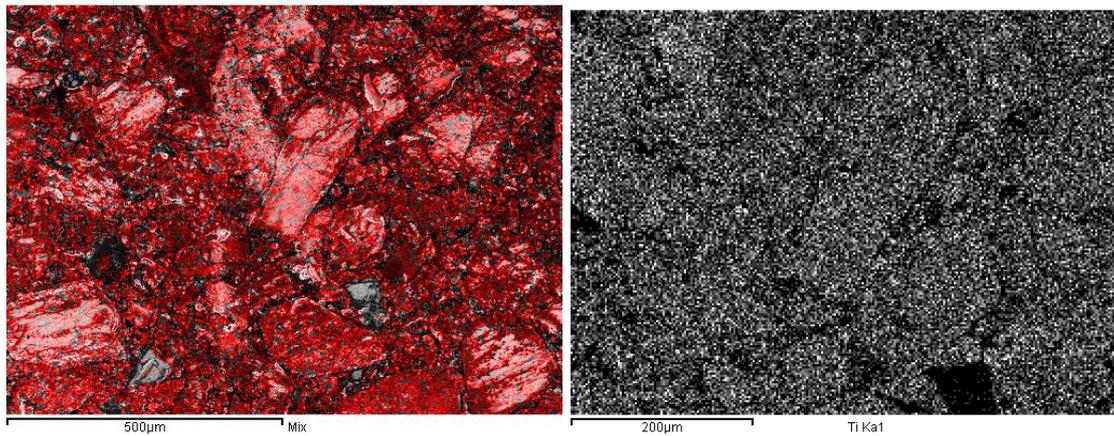


| Element | App<br>Conc. | Intensity<br>Corn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|--------------------|--------------|------------------|---------|
| C K     | 0.05         | 1.2953             | 1.18         | 0.10             | 2.62    |
| O K     | 1.63         | 1.4307             | <b>37.16</b> | 0.93             | 61.97   |
| Mg K    | 0.05         | 1.1402             | 1.51         | 0.06             | 1.66    |
| Al K    | 0.06         | 1.1379             | 1.63         | 0.07             | 1.61    |
| Si K    | 0.11         | 1.1362             | 3.01         | 0.10             | 2.86    |
| Ti L    | 0.87         | 0.8075             | <b>34.75</b> | 1.57             | 19.36   |
| Fe L    | 0.32         | 0.4975             | <b>20.76</b> | 0.68             | 9.92    |
| Totals  |              |                    | 100.00       |                  |         |

## SAMPLE 2 (last session)

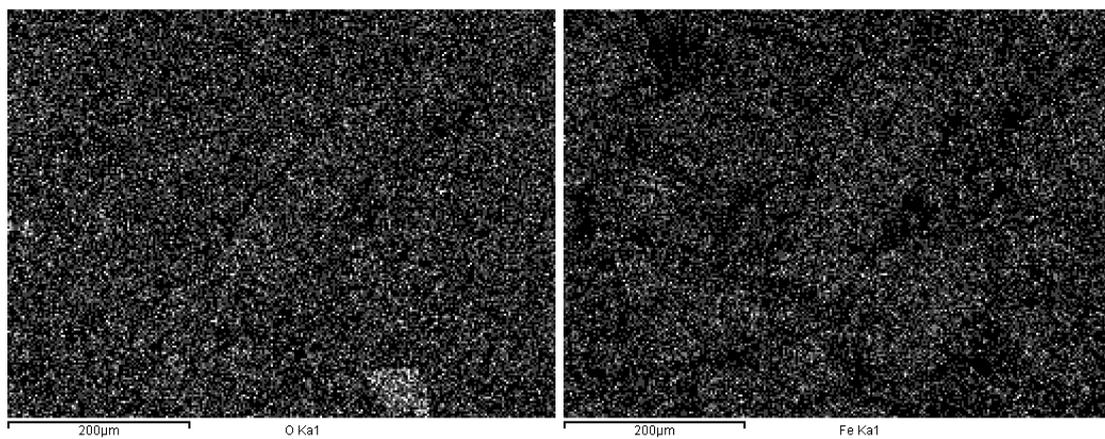


| Element | App<br>Conc. | Intensity<br>Corrn. | Weight%      | Weight%<br>Sigma | Atomic% |
|---------|--------------|---------------------|--------------|------------------|---------|
| C K     | 38.54        | 0.9698              | 35.35        | 0.20             | 55.25   |
| O K     | 17.85        | 0.6160              | <b>25.78</b> | 0.22             | 30.25   |
| Al K    | 0.29         | 0.8718              | 0.29         | 0.03             | 0.20    |
| Si K    | 0.79         | 0.9421              | 0.75         | 0.03             | 0.50    |
| Ti K    | 18.81        | 0.8662              | <b>19.31</b> | 0.13             | 7.57    |
| Mn K    | 1.45         | 0.8041              | 1.60         | 0.08             | 0.55    |
| Fe K    | 15.59        | 0.8191              | <b>16.93</b> | 0.15             | 5.69    |
| Totals  |              |                     | 100.00       |                  |         |



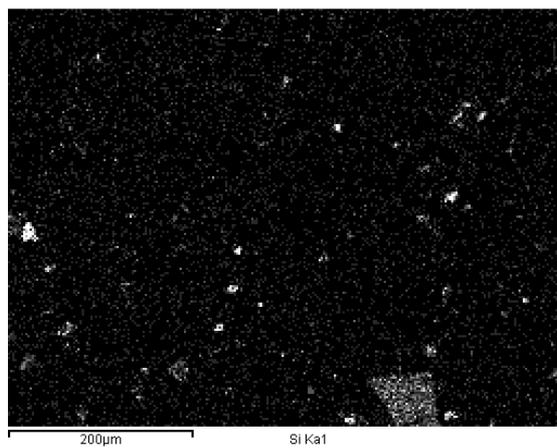
Mix

Titanium



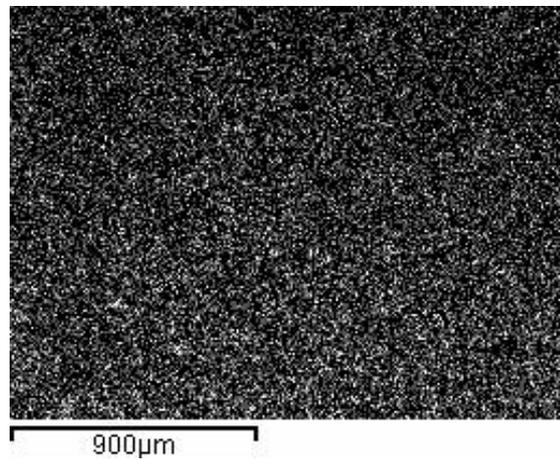
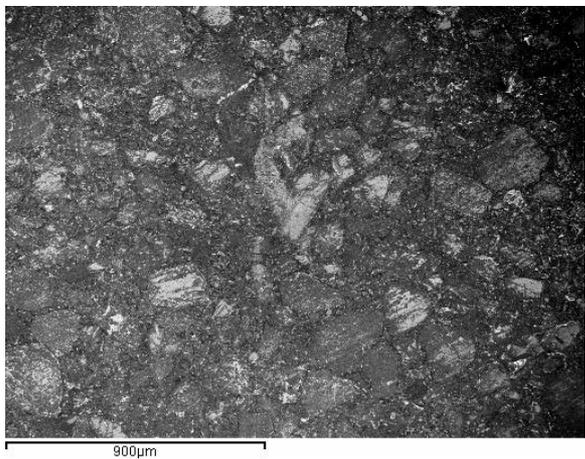
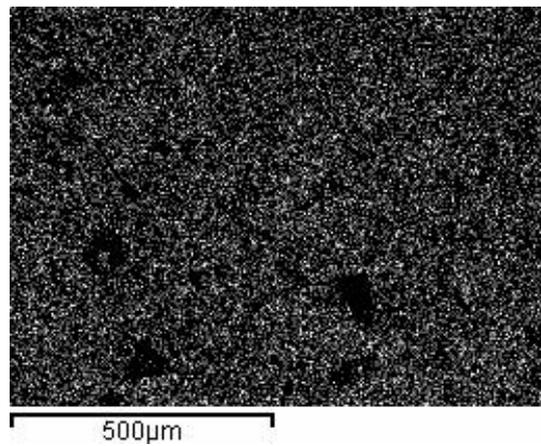
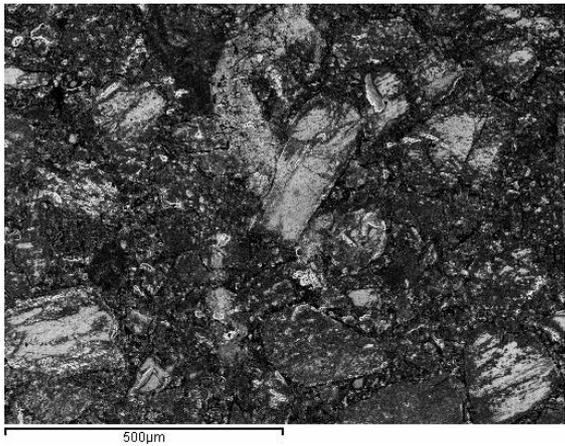
Oxygen

Iron

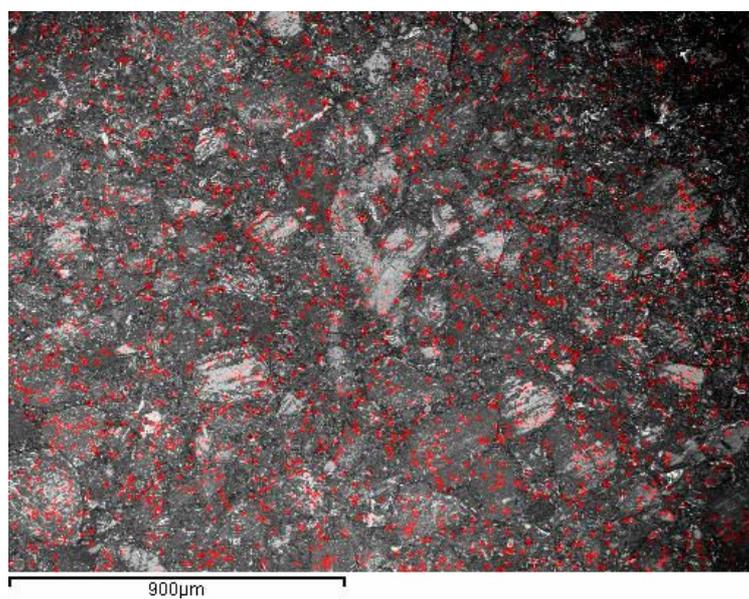


Silicon

**General View of the sample and its titanium content, which is a sign of ilmenite content in white points.**



A lower magnification of the sample 2 and its titanium content.



## ANNEX B - TPR Experiments

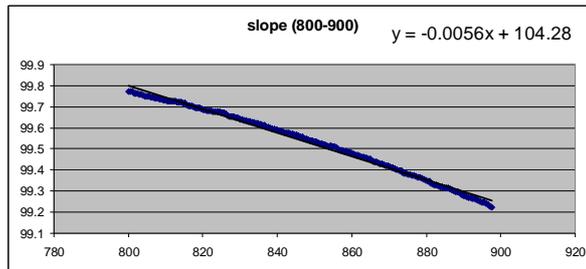
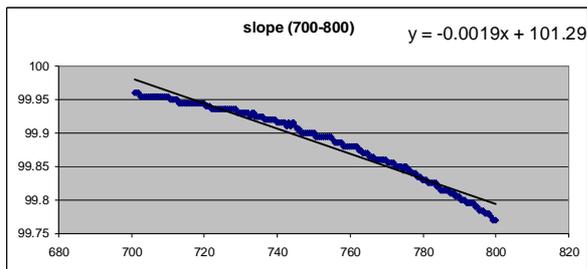
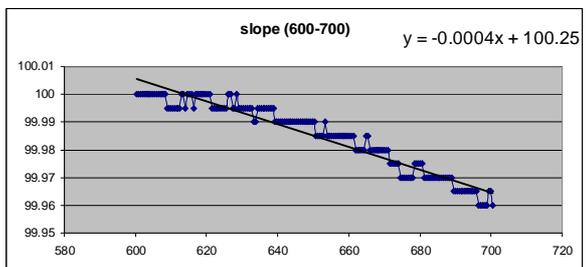
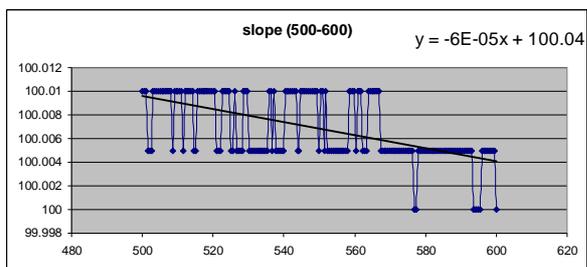
Termogravimetric Analyzer (TGA) guide:

- Open gas N<sub>2</sub> (and H<sub>2</sub> if needed)
- Open compressed air
- TGA ON and wait 5 seconds
- Controller ON and wait until the tub of the TGA is moved.
- PC ON and Screen ON
- Check the PC errors:
  - F2
  - INTRO
  - F12
  - INTRO
  - Do a RESET of the computer
- The computer restart again
- Check on the TGA that the light READY is on and red
- In MSDOS directory write:
- C:\ cd pe (intro)
  - Ta (intro)
- The software will open
- Select Multitasking
- F1
- F5 to move the furnace
- R (raise tube)
- F3 (read weight and put zero value) check it is zero, which means that the sample holder is clean enough)
- INTRO
- Fill (not full) with spatula the sample holder with the Ilmenite
- F5 to move the furnace again
- L (Low the tube)
- F4 (will read the weight with our sample)
- Y (Yes) to make sure this initial measured weight means 100% of weight
- ESC to go to the main menu
- F3 to named the test
- F1 to change the main parameters: scanning rate, initial and final temperature...
- F6 to run the analysis
- F7 to see how the current data is going
- F5
- F1
- F8 to save the data

## TPR Data (from Excel Files)

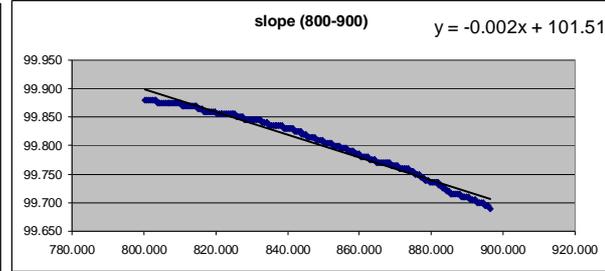
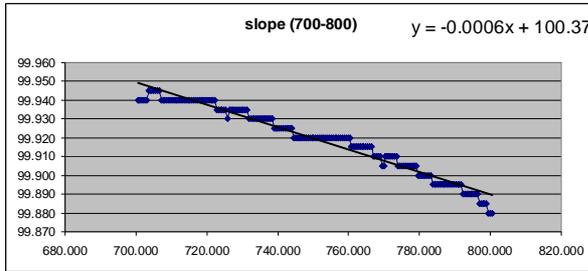
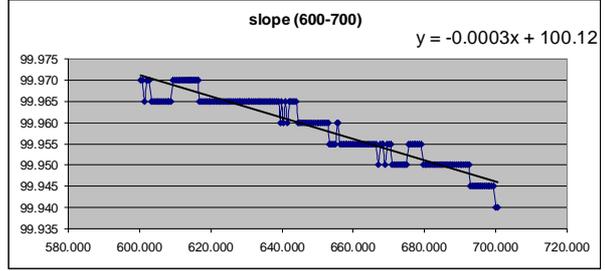
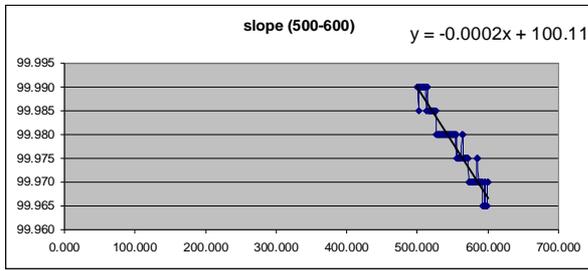
### TEST 3

|  |          |
|--|----------|
| <b>Actual Final Temperature</b>        | 899.5    |
| <b>Minimum Temperature for Display</b> | 100      |
| <b>Sample weight (mg)</b>              | 67.51878 |
| <b>Data Rate(sec/point)</b>            | 3        |
| <b>Actual starting temperature</b>     | 100      |
| <b>Number of data Points</b>           | 1599     |
| <b>Scanning Rate (C/min)</b>           | 10       |
| <b>Input Final Temperature</b>         | 900      |



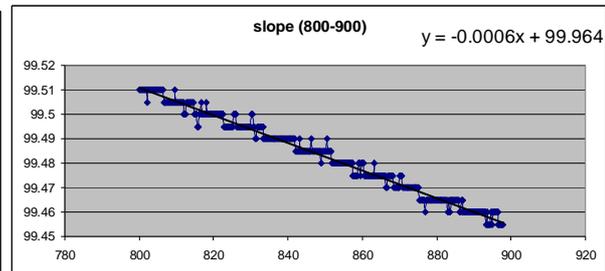
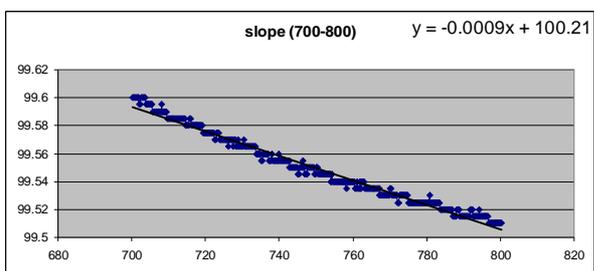
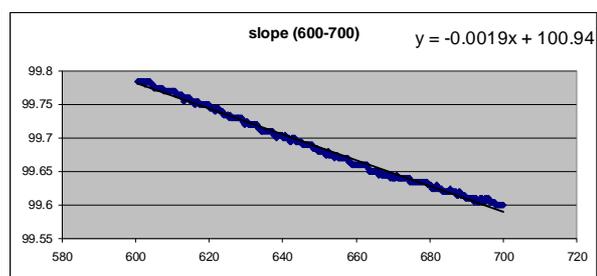
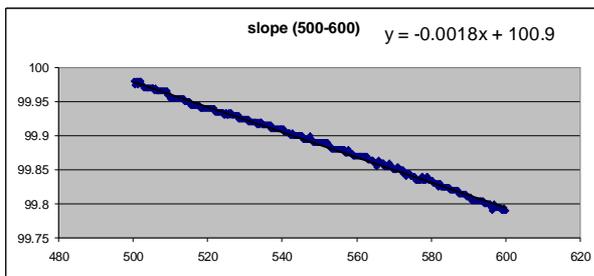
### TEST 5

|  |          |
|--|----------|
| <b>Actual Final Temperature</b>        | 898.500  |
| <b>Minimum Temperature for Display</b> | 100.000  |
| <b>Sample weight (mg)</b>              | 65.893   |
| <b>Curve type</b>                      |          |
| <b>Data Rate(sec/point)</b>            | 1.200    |
| <b>Actual starting temperature</b>     | 100.000  |
| <b>Number of data Points</b>           | 1597.000 |
| <b>Scanning Rate (C/min)</b>           | 25.000   |
| <b>Input Final Temperature</b>         | 900.000  |



**TEST 6**

|  |          |
|--|----------|
| <b>Actual Final Temperature</b>        | 899.6    |
| <b>Minimum Temperature for Display</b> | 500      |
| <b>Sample weight (mg)</b>              | 68.69154 |
| <b>Data Rate(sec/point)</b>            | 3.6      |
| <b>Actual starting temperature</b>     | 500      |
| <b>Number of data Points</b>           | 1665     |
| <b>Scanning Rate (C/min)</b>           | 4        |
| <b>Input Final Temperature</b>         | 900      |



*\*\* By the end of this Master Thesis, the future of NASA's Program Constellation is in doubt. In the new USA's budget, President Obama plans to eliminate the space program's manned missions. However, this is still not completely confirmed. February 2010.*