UPC BARCELONATECH

MASTER of ENVIRONMENTAL ENGINEERING

In Situ X-Ray Photoelectron Spectroscopy Gas-Solid Carbonation of Ultramafic Rocks: Implications for Carbon Capture and Storage

MASTER'S THESIS

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PREFACE AND ACKNOWLEDGMENTS

I enrolled at UPC (Universitat Politècnica de Catalunya- Barcelona Tech) in September 2010. During my four years of bachelor study in Hebei University of Technology which is located in TianJin of China, I was studying major in environmental engineering. I developed an interest in environmental engineering because main courses of this major are relative to the chemistry.

When I was studying in the University, I had an interested in Spanish via a movie, so I chose to study langrage in Spain. After 9 months of Spanish study, I entered the UPC to continue the study about environmental engineering in Master which is the same as my bachelor study.

Thanks to the study in my bachelor period, the knowledge obtained made me understand the contents of Master more rapid and clearly. I also passed all courses in the first three semesters. I paid more attention to the topic of the pollution atmospheric. I preferred to find a thesis topic about air pollution. I thought I had got the best topic after the first class of geoengineering.

First, I would like to thank Professor Ignasi Casanova for helping me to find out an interesting topic promising Master thesis. I also remember the help of all professors who taught me in the past semesters. They didn´t only teach me technology about the environmental engineering but also give me some helps for the life when I just came Barcelona.

Next, I would also to thank the researchers of the Centre for Research in Nanoengineering-UPC. They helped me too much the knowledge about operation of XPS. Especially, I have to thank Montse for operating almost all apparatus of my experiment.

Furth more, I would like to thank my best friends in the UPC such as Jose, Marina P, violeta and my roommate Xi, my friend Yang and so on. The dear classmates helped me achieve the assignments and projects when I couldn´t understand Spanish well. My friends showed consideration for me. I obtained the courage and energy from them. I'm not alone when I was sad for some reason because of their concerns.

Finally, a special thanks to all my family including my dear Mama, my serious Papa, my beautiful aunt and her handsome son. During all my study, they gave me more concerns which supported me in achieving Master thesis.

Abstract

With the increasing carbon dioxide emission in the atmosphere, there has been an interesting interest in CCS (Carbon Capture and Storage). Mineral carbonation was considered as a better option for storage atmospheric CO_2 to slow climate change down. It's a better method for storing CO_2 without re-releasing CO_2 in the atmosphere. The reaction rate of carbonation is too slow to be used at industrial scale under natural conditions containing ambient temperature and pressure. Several pilots were done to study and observer the reaction rate of carbonation with various conditions. In this study, we used the ultramafic igneous rock (such as pyroxene and dunite) containing amounts of magnesium and calcium which could react with atmospheric CO_2 to form stable carbonates into geological formations.

We did the gas-solid carbonation experiment without water-dissolution that was used by amounts of researches in the worldwide to observer change rate of carbonate produced under various CO_2 pressures. By understanding of the previous researches and papers, we knew mineral carbonation in situ has higher carbonation rate relative to rate at $25^O C$ in atoms CO_2 saturated water at 1 bar. We used X-ray Diffraction to understand compounds of the sample in the depth and X-ray Photoelectron Spectroscopy to investigate carbonates produced change in the surface of the samples during the mineral carbonation process. The main aim of this thesis is to evaluate characterization of the sample (including Pyroxene and Dunite) and mineral carbonation procedure in various pressures at 185 $^O C$. The quantitative ratio $[CO_3^{2-}]/C$ for each sample in different reaction conditions has been determined from an analysis of the C 1s spectra of XPS.

The XPS observations showed the same behaviors for the two types of ultramafic igneous rock: the ratio of carbonate to carbon in the surface of the samples at 5 bars is higher than at 1 bar. In addition the ratio of carbonates to carbon after the heating treatment decreases a little, and then the value would increase after the carbonation procedure. That means the carbonates were removed by the heating treatment.

Key words

Gas-solid carbonation　XPS　XRD　Carbon Dioxide　CCS

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Chapter 1

Introduction

Content

1.1 Introduction of actual situation of climate change

With the intensification of global warming, the issue of carbon emissions causes more and more attention in recent years. Global warming is a phenomenon of climate change .There is rise in sea level, desertification and El Niño from climate change. Global warming is an indisputable fact, which seriously affected people´s normal living and development of human society. In addition to natural factors (such as oceanic circulation, variations in solar radiation received by Earth plate tectonics and volcanic eruptions and so on), human activities (direct or indirect human activities) play an important role in climate warming, especially anthropogenic CO_2 emission. [1].

Most of the increasing in global average temperatures which was observed and reported by the IPCC report climate change 2007 (working group I: The Physical Science Basis) since the mid-20th century is very mostly due to the observed increase in human greenhouse gas concentrations.

As we known, the most important gas of the greenhouse gas is Carbon Dioxide which derived from burning of fossil fuel and then that has been increasing the effect by human being.

Carbon dioxide (CO_2) concentrations in the atmosphere have been increasing over the past century compared to the rather steady level of the preindustrial era (approximately 280 parts per million in volumes, or ppmv). The 2005 concentration of CO2 was about 379 ppmv.

The data of concentration of CO2 in April 2012 was shown by Earth System Research Laboratory. In addition the current CO2 concentration is approximately 396.18 ppmv in 2012, is about 41.4% higher than in the mid-1800s, with the fastest growth rate in the recent year (393.28ppmv in 2011, the growth rate is 2.9 ppmv/year from 2011 to 2012). This is a quite rapid increasing rate.

1.2 Methods to reduce atmosphere CO_2

As a result of the effects of the primary changes such as change in temperature, rainfall, sea levels, and increased frequency of extreme weather events (of a physical nature), the consequences manifestations which derived from the natural changes mentioned above are more varied, containing social, ecological, and economic impacts.

In order to mitigate atmospheric CO_2, a group of policy methods was published in the last century that is Kyoto Protocol by United Nations Framework Convention on Climate Change (UNFCCC).

More and more research centres and scientific communities have interesting in the technology of removal CO_2 in the atmosphere for avoiding climate warming in the future. Various researchers studied technologies about Carbon Dioxide Removal as schemes for collection and disposal of CO_2 have been studied recently.

At first we have to understand the options of technology of the Carbon Dioxide Removal.

Carbon Dioxide Removal refers to a number of technological methods which eliminate the concentration of atmospheric CO_2. Various technological methods were studied by the researchers before. The most important options are introduced as follows. The main technologies involve in bio-energy with carbon capture and storage, biochar, direct air capture, ocean fertilization[2] , enhanced weathering and carbon capture and storage.

The goal of the technologies of mitigation CO_2 is the same as the politic protocol´s (Kyoto protocol from United Nations Framework Convention on Climate Change) to reduce CO_2 concentration in the atmosphere. It was pointed out in the IPCC Fourth Assessment Report by the Intergovernmental Panel on Climate Change (IPCC) as a key technology for reaching low atmospheric carbon dioxide concentration targets.

1.3 Carbon Capture and Storage

With stronger effect of global warming and the continued growth in temperature caused by increasing CO_2 in the atmosphere, more and more countries are facing greater pressure to cut their CO_2 emissions down.

The capture and storage of Carbon Dioxide (CO_2) from burning of fossil fuel obtained attraction as a means to deal with climate change. Now the main research centre worldwide and a number of researchers pay more attention to decrease CO_2 emission. CCS was seen as a key technology to reduce CO_2 emission in the atmosphere. [3] The concept of CCS refers to attempting to avoid the release of large quantities of CO_2 into atmosphere from fossil fuel in power generation and other industries by capturing CO_2, transporting it and lastly pumping it into underground geologic formations to safely sequestrate it away from the atmosphere. [4]

Mineral storage- also known as mineral carbonation, in this process, carbon dioxide is exothermically reacted with available metal oxides, which is for making stable carbonates. This option is a natural process over many years and is responsible for a great amount of material surface. We have gained a conclusion that if reacting temperature and/or pressures are increased, the reaction rate of mineral carbonation will be made faster than the natural speed. [5]

1.4 Plan of the present work

Nowadays as result of the development of industry, CO_2 emission in the atmosphere became a more serious problem. We know the actual situation of atmospheric CO_2 (in 1.1).A summary of the methods used including politic methods and technological options is presented (in 1.2).

Among of various technological options designed to reduce atmospheric CO_2, Carbon Capture and Storage played a more important role and is induced (in1.3). The basic concepts are induced in the first part Introduction.

The structure of the present work as follows: The goal of this paper will be presented in next part (chapter 2). The idea of this experimental design derived from a previous paper shown in chapter 3. We explain why and how we designed this experiment in chapter 3. The whole experimental method and materials used for the experiment are presented in chapter 4. In chapter 5 we discussed the results. Finally we present the conclusions in chapter 6.

Chapter 2

Objective

With the development of industrialization, more and more anthropogenic CO_2 produced by human direct or indirect activities input to the atmosphere has obviously increased CO_2 concentration in the atmosphere and destroyed people´s normal living. The increasing of atmospheric CO_2 concentration could enhance climate warming in the worldwide. Through previous researches from a few of scientists, mineral carbonation has been more focused on which is a storage option to store atmospheric CO_2 to stable mineral carbonate such as calcite and magnesite into geological formation such as igneous ultramafic rock including peridotite, olivine and so on. Ultramafic rocks contain Ca, Mg-bearing and others cation metal ion to react with atmospheric CO_2 for forming stable carbonates.

We did an experiment by injection of CO_2 (gas) into geological formations (solid) where the elements required for carbonate-mineral formation remain to be resolved. Carbon sequestration by the mineral formations is a method of elimination of CO_2 which naturally involve in chemical element Magnesium and Calcium containing minerals with atmospheric CO_2 to form stable carbonates. There are many unique advantages, the most noble is the fact that carbonate has a lower energy state than atmospheric CO_2, that is why mineral carbonation is thermodynamically favorable and occurs naturally for example the weathering of rock over geologic time periods. In addition, the raw materials such as magnesium based mineral are abundant in nature. Finally the carbonates produced during the mineral carbonation procedure are unarguably stable and thus re-release of CO2 into the atmosphere is not a problem for this technology.

In the thesis we investigate characterizations of the compounds of Pyroxene and Dunite from Cabo Ortegal in Galicia of Spain by X-ray diffraction. Amounts of pilots about mineral carbonation (CCS) react between igneous ultramafic rocks and CO_2 in gas with water-dissolution treatment or acid treatment for increasing Kinetic rate in order to mineral carbonation rate before carbonation process, so the reaction formation is gas-liquid. Here our experiment was done by heating treatment without water-dissolution before the carbonation reaction. The formation of the reaction is like gas-solid. This experiment was designed by changing various conditions including temperature and pressure. Through paper in situ carbonation of peridotite for CO_2 storage published, we knew the rate of carbonation optimized at $185^{O}C$ and 150 bars CO_2 pressure. The

experiment done was designed be this result from the paper above. We wanted to observer the ratio of carbonates to carbon during the carbonation procedure at 185^OC and at various CO_2 pressure including 1 bar and 5 bars. The results surveyed were that difference of carbonate produced at various conditions including heating the sample at 185 ^{O}C and up pressure to 1 bar and 5 bars.

Chapter 3

Literature Review

Dealing with the issue of global climate change is currently one of the biggest challenges in wild world range. Carbon dioxide is an important contributor to the earth´s greenhouse effect and anthropogenic use of fossil fuels caused a rise in atmospheric CO2 concentration. [6]

Carbon dioxide (CO_2) concentrations in the atmosphere have been increasing over the past century compared to the rather steady level of the preindustrial era (about 280 parts per million in volume, or ppmv). Fig.1 shows the change in CO2 emission by region. The increasing rate of CO2 emission of developing countries is faster than the developed countries (2008-2009).
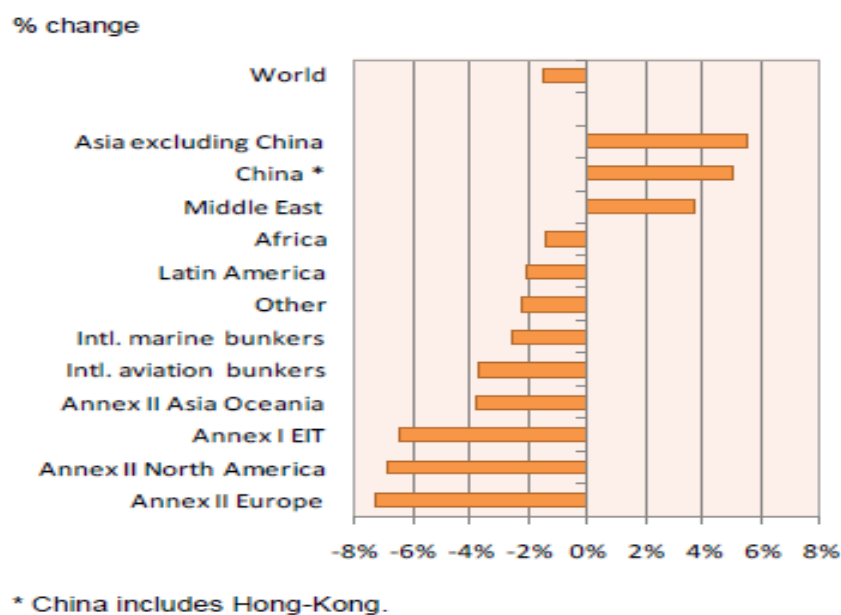
Figure 1 Change in CO₂ emission by region (2008-2009)
Key point: Between 2008 and 2009, CO₂ emissions increased significantly in Asia, China and the Middle East, while declining in the world as a whole(China includes Hong-Kong)[7]

Global climate change has increased greatly in number and quality over recent decades thereby improving the scientific understanding of past, present and future climate change.

Climate change is expected to have significant impacts on whole world resources. [1]

Figure 2. Global average radiative forcing (RF) estimate and ranges in 2005 for anthropogenic GHGs (IPCC)(RF measured the effect of human activities on the climate change on the climate system.)

Global average radiative forcing (RF) estimated by IPCC was shown in Fig.2. The information could be obtained that Carbon Dioxide (CO_2) is the most important anthropogenic GHGs. So stabilizing the concentrati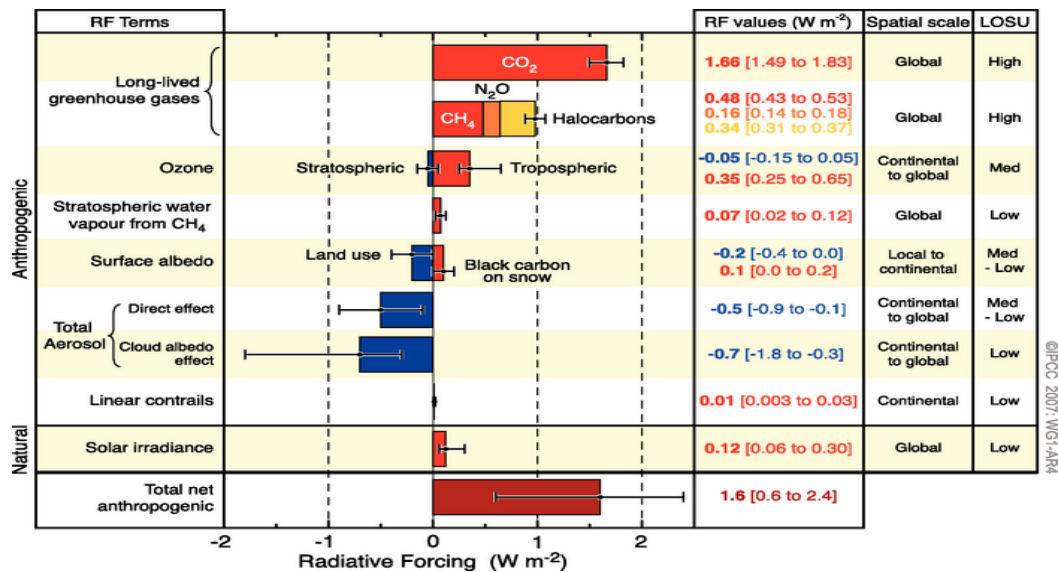on of atmospheric CO_2 would ultimately require the effective elimination of anthropogenic CO_2 emission. The anthropogenic CO_2 emission derived from fossil fuel combustion of the human activity particularly in the developing country during the industrial process.

Through the descriptions of the situation of climate change (particular climate warming the same as temperature increasing in the whole world wide), we understand the serious matter about climate warming.

The disposal of carbon dioxide is an important technological project. It appears that the disposal issue is the more difficult one. Now there are several possible options to resolve this problem to store CO_2 into the geological formation such as depleted oil and field [8], coal bed[9], and saline aquifers[10]; ocean disposal[11], terrestrial sequestration[12], mineral carbonation[13]and biological fixation[14]. All of the proposed options involve the long term storage of CO_2 in solid, liquid or gaseous form. A large number of CO_2 produced from the plant was injected and stored in the mineral formation to be permanent without re-release in the atmosphere. The most concern of this option is the possibility of an accidental release, a possibility with serious consequences, as demonstrated in past natural disasters.[15]

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Mineral carbonation was observed as a great potential option to store CO_2 gas to form stable solid carbonate such as calcite($CaCO_3$) and Magnesite($MgCO_3$)[16]. So Carbon Dioxide mineral sequestration is an increasing interest of this topic. The main idea of this plan involves in capturing and injecting CO_2 into a target geological formation.

The reactivity was proved to basalt weathering that played an important part in exchange of CO2 between mineral solid in the earth and the atmosphere. There is an abundance of suitable mineral that involves in magnesium silicate such as serpentine and olivine which contain high concentration of MgO, while also pyroxene is a potential material for CaO and MgO. So the main reactivity of the mineral carbonation during the chemical process general as follows:

$$(Mg, Ca)_x Si_y O_{x+2y} + x\ CO_2 \longrightarrow x\ (Mg, Ca)\ CO_3 + y\ SiO_2$$
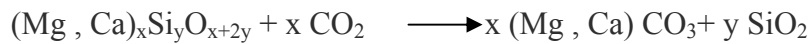
As previous studies of mineral carbonation in the lab, we knew that kinetics is slow for the carbonation rate unless geological formation reactants such as olivine or serpentine are ground to powder, heat-treated and held at elevated pressure and temperature.

Mineral carbonation is different in reaction speed in situ and ex situ by the results of previous researches.

The rate of natural carbonation of tectonically mantle peridotite in the Samail ophiolite is surprisingly rapid. [17].In this paper, they proposed and evaluated ways to increase CO_2 uptake in site in tectonically exposed peridotite massifs. An additional increase in the carbonation rate, by a factor of $\geq 10^6$ approximately, could be achieved by rising the temperature of the peridotite and injecting CO_2-rich fluids. There is an optimal temperature for peridotite carbonation. They obtained that the rate of carbonation is optimized for example, at 185 ^{O}C and 150 bars CO_2 pressure. The cause of increasing carbonation rate is that the chemical potential driving the reaction is reduced as the temperature approaches the equilibrium phase boundary for serpentine or carbonate mineral stability with heating from low temperature speeds the diffusive kinetics of hydration and carbonation. The rate of carbonation obtained is optimized at for example, 185°C and 150 bars (shown in Figure 3)
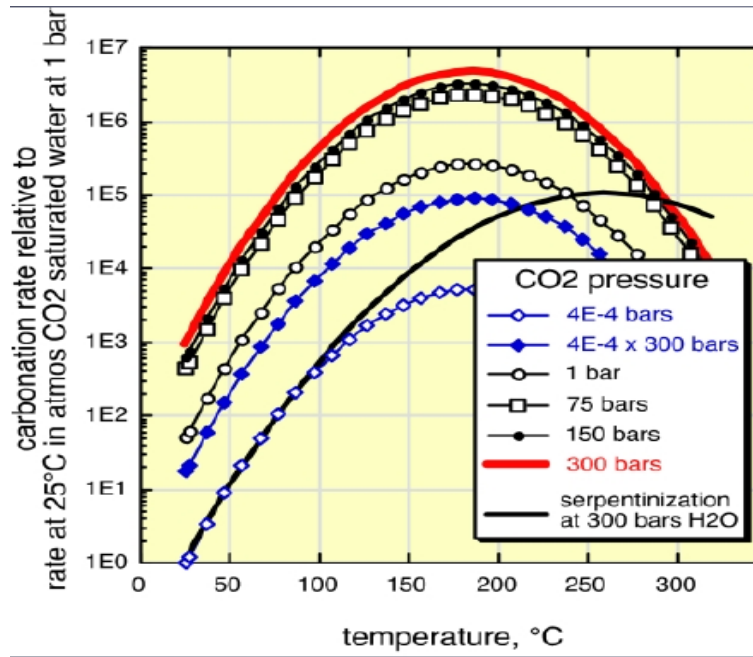
Fig. 3 Rate of olivine carbonation (lines and symbols) and serpentinization (black line, no symbols) as a function of tempurature and pressure compared with the rates at 25°C for surface water equilibrated with the atmosphere at 1 bar. A range of curves are showed for carbonation, with a single curve for serpentinization of olivine saturated in aqueous fluid at 300 bars.

By fig.3, we knew that heating and raising the partial pressure of CO2 can increase the carbonation rate. The design of our experiment derived from this paper.

Chapter 4

Materials (Infrastructure) and procedure (method)

Content

4.1 X-ray Diffraction

As known, about 95% of solid material can be described as crystalline. When X-ray interacts with a crystalline substance (Phase), one gets a diffraction pattern. It means every crystalline gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others.

XRD analysis was used basis on this theory that the X-ray diffraction pattern of a pure substance is like a fingerprint of the substance for the solid material. The main use of powder diffraction is to identify compounds in a sample by a search/match procedure. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin \theta$), the process is shown in Figure 4. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.
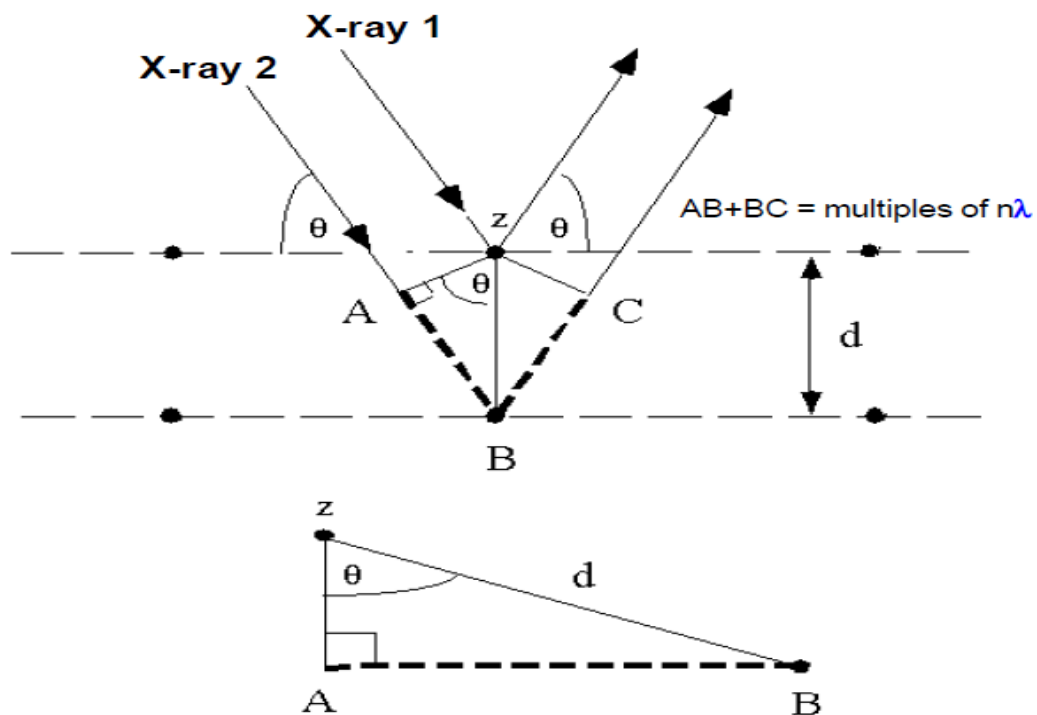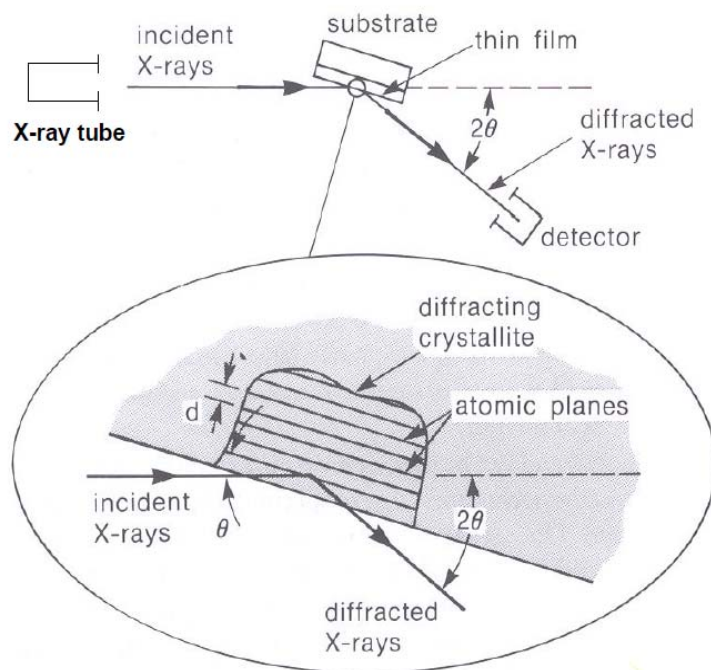
Figure 4   The theory of X-ray Diffraction nλ=2d sin θ

1) Production

2) Diffraction

3) Detection

4) Interpretation

Figure 5 Basic components of XRD equipment

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. Figure 5 shows a operating principal of diffractometer system.

In our research, we used the X-ray diffractormeter from Centre for Research in NanoEngineering (UPC-BarcelonaTech) to identify generally compounds of the samples. The infrastructure is showed in Figure 6.

Figure 6 X-ray diffraction infrastructures from crne in UPC-BarcelonaTech

4.2 X-ray Photoelectron Spectroscopy

The XPS (known as ESCA that is Electron Spectroscopy for Chemical Analysis) plays an important role in the chemical analysis of the surface of materials. It is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, paints, papers, inks, woods, plant parts, make-up, teeth, bones, medical implants, bio-materials, viscous oils, glues, ion modified materials and many others.

X-ray photoelectron spectroscopy is widely used for two basic purposes:

Firstly the determination of the chemical state of surface atoms based on the energy chemical shift induced in core levels by chemical bonding.

Secondly the determination of surface chemical composition was observed by using peak area ratios.

The theory of the XPS analysis is based on the work of the Ernest Rutherford. (the ErnestRutherfordwas a New Zealand chemist and physicist who became known as the father of nuclear physics)[1]. There are relatively few of these types of XPS systems, a few , special design, XPS instruments can analyze volatile liquids or gases(no only material solid) at low or high temperatures o material at roughly 1 torr vacuum. Figure 7 show the operating principal of XPS.
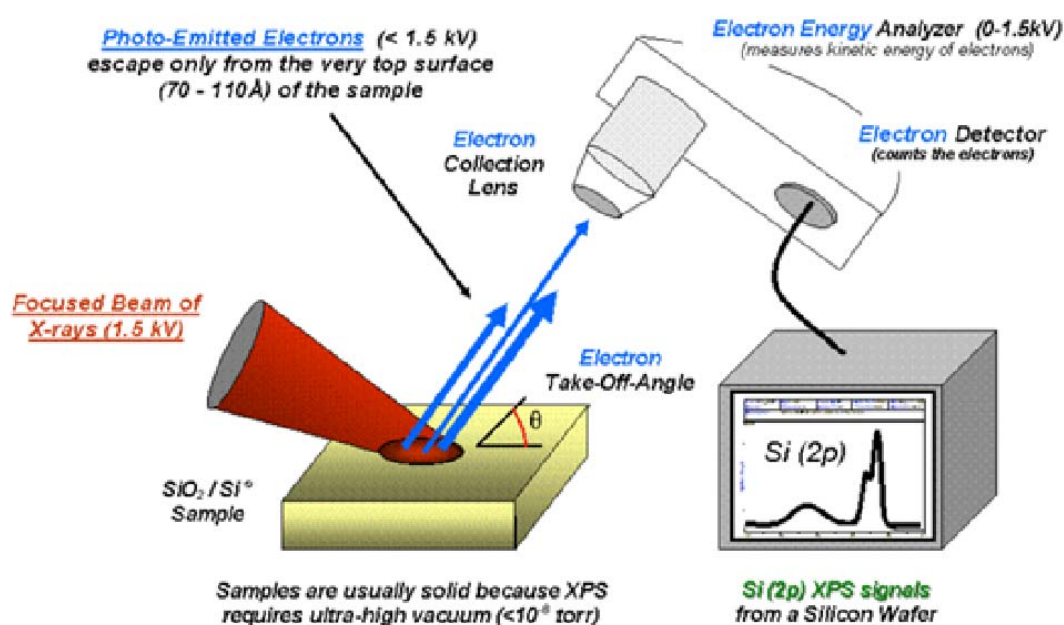

Figure 7 Operating principal of X-ray Photoelectron Spectrascopy

The energy of an X-ray with particular wavelength is know, the electron binding energy of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford (1914):

Energy binding = E photon – (E kinetic + Φ)

Energy binding is the binding energy (BE) of the electron

Energy photon is the energy of the X-ray photons being used

Energy kinetic energy of the electron as measured by the instrument

Φ is the work function of the spectrometer, isn't the material.

Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exist in or on the surface of the material being analyzed. In other word, the each characteristic set of XPS peaks is used to identify directly each element in the surface of the material by the various binding energy.

We used this theory of XPS to analyze characterization of the samples during the reaction procedure to observe the change of carbonate produced in the carbonation reaction. The XPS used is from crne too, showed in Figure 8. The data analysis was presented by program CasaXPS.
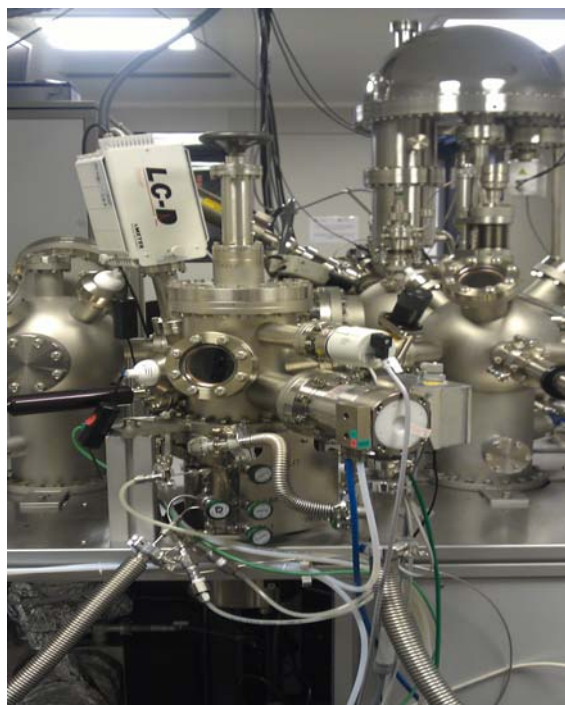

Figure 8 The Infrastructure of XPS in crne(UPC-BarcelonaTech)

The instrument XPS used of the Centre for Research in Nano-Engineering contains the following components:

Ultra high vacuum multi-chamber system with a load lock and storage chamber connected to a:

X-ray photoelectron spectroscopy chamber with a nine channel detector and possibility of performing z-profiles.

AFM and STM microscopy chamber.

Independent preparation chamber.

High pressure, high temperature cell for gas treatments equipped with a mass spectrometer.

The carbonation process was reacted in high pressure chamber connected with partial CO_2 pressure. The characterization in the surface of the sample was analyzed by XPS.

4.3 Characterization basic of the samples

The samples used were from Cabo Ortegal in Galicia of Spain for this study. Cabo ortegal is a location in the autonomous community of Galicia in Spain. It's a part of the Spanish Atlantic coast. Ortegal also get international attention of geological complexion. A number of materials came from the collision of continental fragment of the Baltic and North Atlantic. There are basic rocks, ultrabasic, gneiss or eclogites. (stones very hard and very resistant to erosion) in the surrounding of Cabo Ortegal. The ultramafic igneous rocks are interested in this study. Through previous researches, we believed that the rocks of the Ortegal contain a wide range of chemical and mineral element composition, and special characterization including substantial proportions of calcium and magnesium. The advantage of the rock of the Ortegal will be given to geographical distribution and abundance of such formation, in order to provide some preliminary data on feasibility and potential application of the research results. Thanks to such variety of the rocks, we selected the sample from Cabo Ortegal. So finally we used the Dunite and

Pyroxene which are from Ortegal as the experimental sample for the research(bulks of the sample are shown in Figure 9).

Dunite   Pyroxene

Figure 9 Bulk of the sample rock dunite and pyroxene from Ortegal

The mineral assemblage of dunite is greater than 90% olivine, with minor amounts of other minerals such as pyroxene, chromite and pyrope. Dunite is the olivine-rich member of the peridotite group of mantle derived rocks.

The pyroxenes are a group of important rock-foeming inosilicate minerals found in many igneous and metamorphic rocks. En general pyroxenes have the formula XYZ_2O_6, $X=Mg^{2+},Fe^{2+},Mn^{2+},Li^{2+},Na^+,Y=Al^{3+},Fe^{3+},Cr^{3+},Ti^{4+},Mg^{2+},Fe^{2+},Mn^{2+},Z=Si,Al^{3+},Fe^{3+}$.The common form is $(Ca,Mg,Fe)_2Si_2O_6$.[18]

4.4 Procedure of the experiment (Method)

4.4.1 Preparation of samples for analysis

First we have to know compounds of the two types of samples generally by X-ray Diffraction. We have used XRD previously to make a qualitative analysis for the sample in the depth. The results of the analysis are shown in Figure 10 and Fig.11 to understand better components of Dunite and Pyroxene from the CaboOrtegal.

Figure 10 shows the compounds of Dunite include tremolite,dolomite,augite(aluminian), lizardite, halloysite, ferrosilite, magnesium silicate.

Dolomite is found out in the observation of Dunite by using X-ray Diffraction. It´s a carbonate mineral composed of calcium magnesium carbonate $CaMg(CO_3)_2$. The carbonate mineral dolomite is a pre-existing in the Dunite.
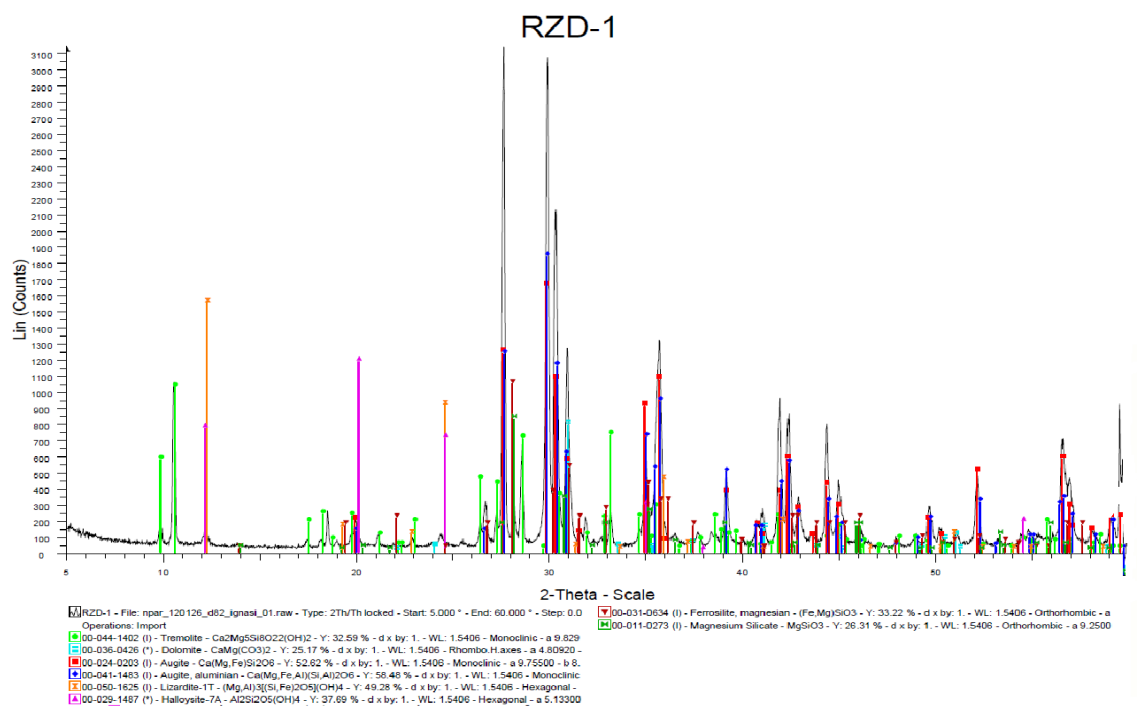
Figure 10 Qualitative analysis of Dunite by X-ray Diffraction

The compounds of Pyroxene are showed in Figure 11 as follows. The components contain that tremolite, Augite, Augite, aluminian and Lizardite.
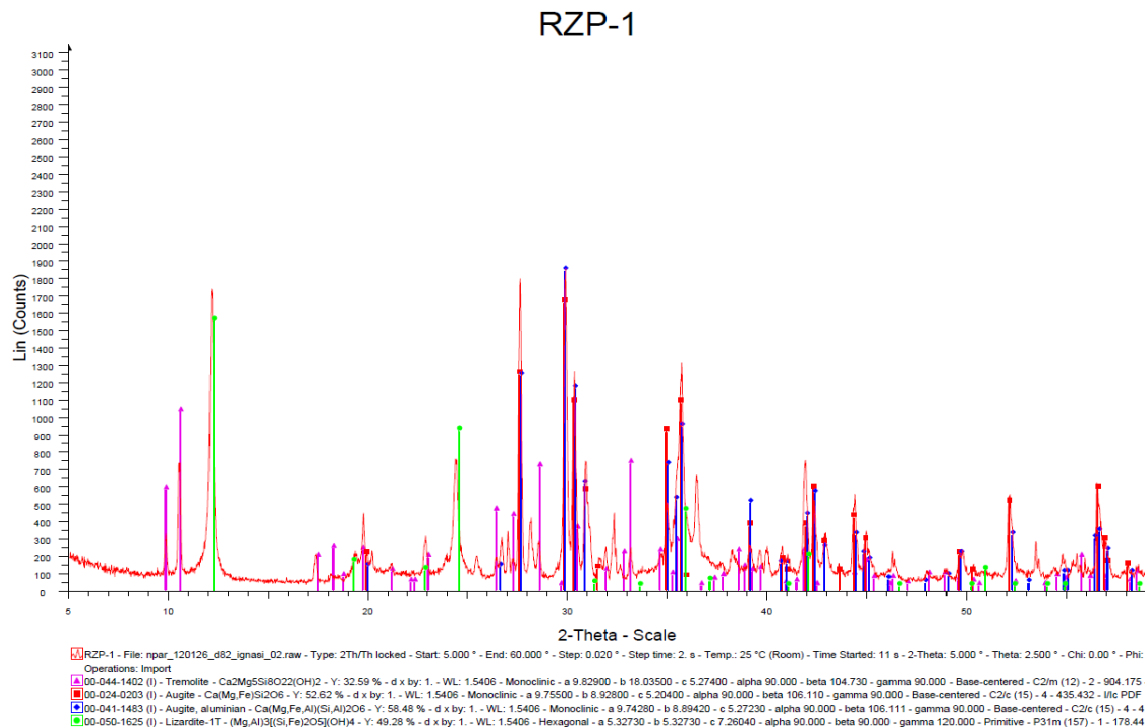

Figure 11 Qualitative analysis of Pyroxene by X-ray Diffraction

Through the figures above, we can understand more the compounds of the two different samples in our experiment. The compounds of each sample are presented in table 1

Dunite		Pyroxene	
common name	chemical name	common name	chemical name
Tremolite	Ca2Mg5Si8O22(OH)2	Tremolite	Ca2Mg5Si8O22(OH)2
Dolomite	CaMg(CO3)2	Augite	Ca(Mg,Fe)Si2O6
Augite	Ca(Mg,Fe)Si2O6	Augite,aluminian	Ca(Mg,Fe,Al)(Si,Al)2O6
Augite,aluminian	Ca(Mg,Fe,Al)(Si,Al)2O6	Lizardite	(Mg,Al)3[(Si,Fe)2O5](OH)4
Lizardite	(Mg,Al)3[(Si,Fe)2O5](OH)4		
Halloysite	Al2Si2O5(OH)4		
Ferrosilite,magnesian	(Fe,Mg)SiO3		
Magnesium,silicate	mgSiO3		

Table 1 The comparison of the compounds of the two samples by X-ray Diffraction

4.4.2 Main experimental procedure

The samples were extensively characterized with classical analytical methods, including powder X-ray diffraction on polished thin sections. For examination with nanoscale techniques, X-ray photoelectron spectroscopy and Infrared spectroscopy tools and working conditions crucial. Fresh Pyroxene and Dunite sample surfaces were obtained by powdering them until they fractured into smaller pieces.

By using mechanism treatment the big bulk of the rock had been broken into smaller pieces. The bulks of the rocks were crushed to produce the finest size fraction of material possible. The stamp crushing process was repeated until the powder of the material was sufficient tiny for doing the experiment.

Figure12 Hydraulic press SPECAC15 model

And then powdered material was pressed into pellets with hydraulic press SPECAC15 model works with the high pressure to get the powder together as a pellet finally. At last, we got the tiny samples (shown in Figure 13) for the analysis of XPS. We had to put the samples in the seal box (Fig.14).


Fig.13The two sample Pyroxene and Dunite in dust, RZP-Pyroxene and PZD-Dunite(on the left).

Fig.14 Final samples for the XPS experiment(on the right).

This step was in order to avoid contaminating the samples by gas pollution of the air take for example CO_2, SO_2, dust that all can react with the samples.

After preparation of the samples, we entered in main experiment step carbonation reaction and XPS analysis in the surface of the sample. As the design and objective of this thesis we have discussed before, pre-treatment for the carbonation is heating treatment. We heated the samples in turn at $185^{\circ}C$ for 2 hours in High Pressure Chamber (HPC showed in Figure 15). We had to observe X-ray Photoelectron Spectra analyzed by XPS in the chamber showed in Figure 15 before the heating and after the heating to know the relative concentration of each chemical state. XPS analysis was working during 2hours. At last, before carbonation reaction with partial CO2 at 1 bar (5 bars) for 2 hours, the last step is to check chemical state of the sample in XPS chamber.
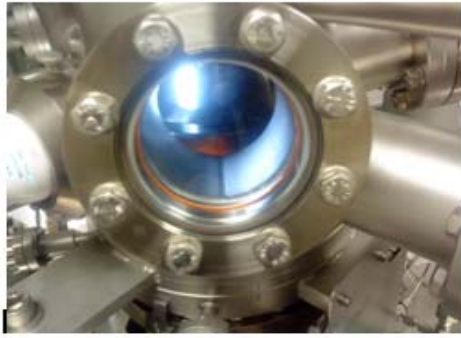
High Pressure Chamber
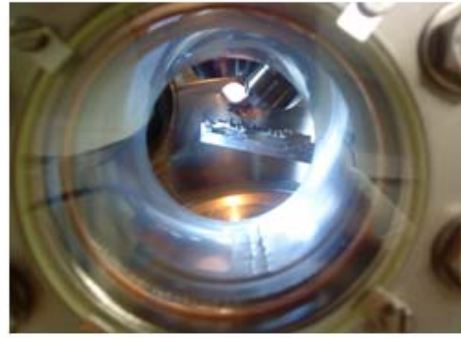
XPS chamber

Figure 15 High Pressure Chamber used for heating treatment and carbonation and XPS chamber is used for analyzing chemical state in the surface of materials.

Chapter 5

Results and Discussion

Content

5.1 Temperature at 185^OC(483K) and Pressure at 1 bar

5.1.1Sample Pyroxene

5.1.2 Sample Dunite

5.2 Temperature at 185^OC(483K) and Pressure at 5 bars

5.2.1Sample Pyroxene

5.2.2Sample Dunite

5.1 Temperature at 185°C (483K) and Pressure at 1 bar

5.1.1Sample Pyroxene

Survey-scan X-ray photoelectron spectra for the samples compositions, obtained by XPS analysis, showed in Figure 16. The XPS peak for the constituent elements in the sample are followings, C1s-284.8eV, O1s-530.5eV,Si2p-103.15eV,Mg2s- 89.17, Ca 2p-350eV,Fe-709.79eV and Si2s-154eV.
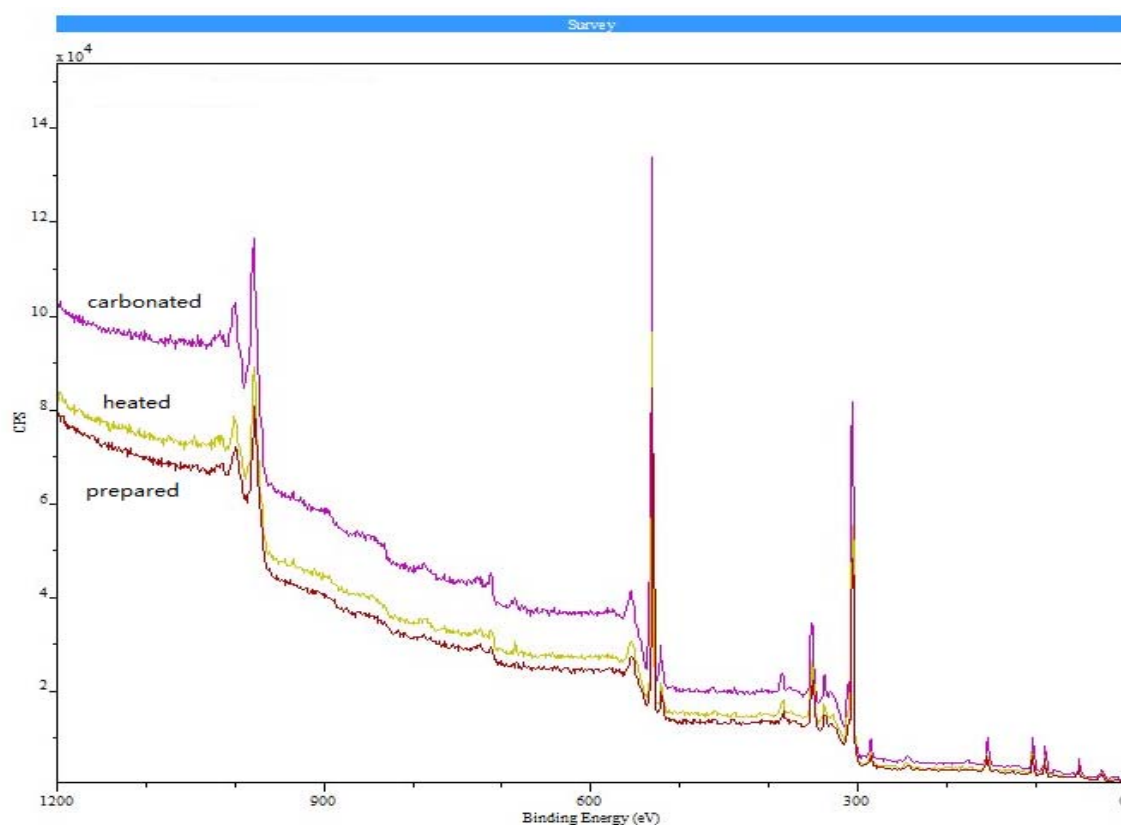
Figure 16 XPS survey scan for the Pyroxene carbonation at 1 bar

The high resolution C1s spectrum for the sample is showed in Figure17. The figure following shows the C 1s spectra of the two samples during experimental procedure, such as spectra of the prepared one without any treatment, heated sample at 185°C (483K) for 2 hours and carbonated one at 24-25 °C and carbonating it at 1 bar for 2 hours.

First, we have to observe the chemical state existed in the surface of the samples by the data from the XPS. We focus on the photoelectrons spectrum with respect to the binding

energies of the electrons is photoelectron peaks. The survey analysis was carried out in a common binding energy range of 1-1200eV. XPS survey scans during experimental procedure, shown in Fig.16, were qualitatively the same. Subtle differences in the relative atomic concentration of each element peak were observed. The main peaks observed in the survey scans of the sample Pyroxene are C1s spectrum of XPS.

In our case, the C 1s peak is more important than the others element for detecting carbonation process. We have to observer the variety of carbonate content of each sample. In the study, we focus on observing the C1s peak of XPS. The C 1s spectrum presents the feature of Carbon during the experiment. Although the others element's spectra has been observed by the XPS, they aren't shown here.

XPS analysis for the carbonation procedure of Pyroxene was observed. The most important C1s peak is indicated in Fig.17.
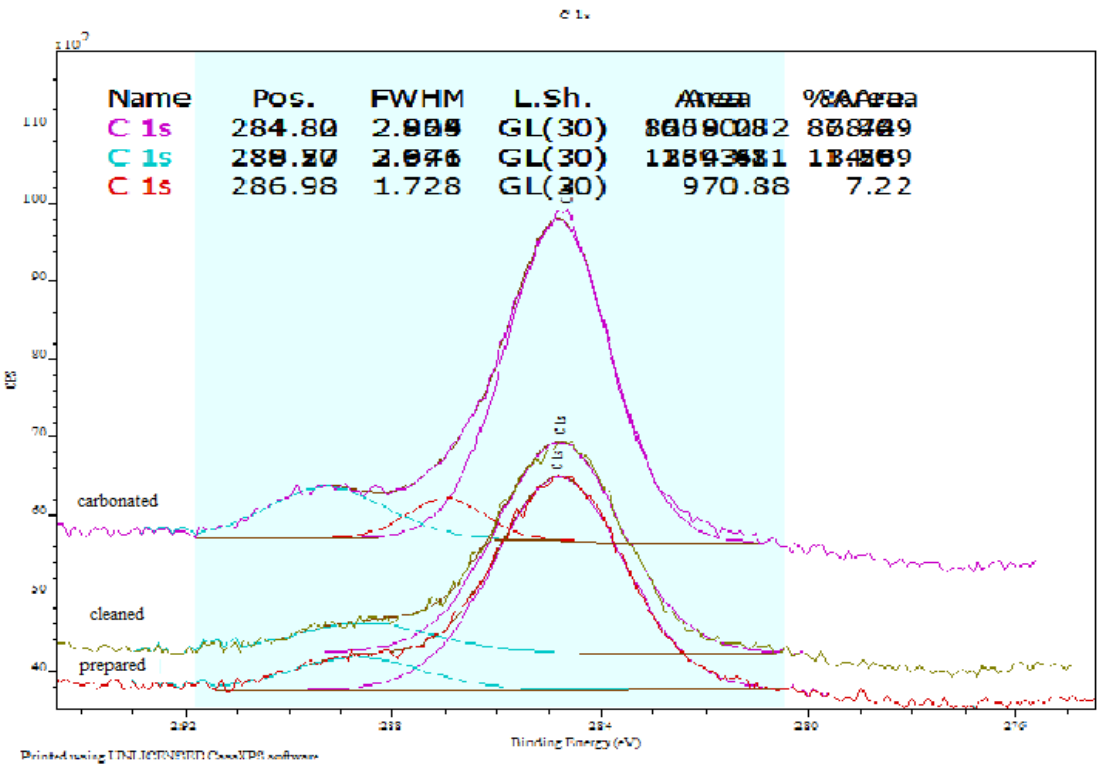

Figure 17 A comparison of XPS analysis for Pyroxene at 1 bar. The C1s peak is indicated.

The band's scope of C1s spectra of the prepared Pyroxene is from 280 eV to 291.5 eV is shown in Fig.A1. There are two positions of the scan of the C 1s XPS peak in the fig. A1 that are 284.80eV and 288.70eV.XPS confirmed the presence of carbon (Binding

Energy of C1s is 284.5 eV) [19]and carbonate (Binding Energy of C1s is nearly 288.5 eV)[19].

For the quantitative analysis, table 2 shows the atomic concentration results from the XPS of each chemical state. We can note relative intensities of these peaks. Surface atomic concentration ratio of Carbonate/Carbon (CO_3^{2-}/ C) is 0.157 by the calculation of the ratios of the area in the table and formula as follows

Ratio (carbonate/ carbon) = Area of carbonate (at 288.7 eV) / Area of carbon (at 284.8 eV)

The sample was needed to clean before carbonation reaction. The spectra of the C 1s peak was showed in the fig.A2, qualitatively the same as the prepared one, although subtle differences in the atomic concentration. The chemical state of the cleaned one was found as the same as the prepared one that are C (carbon at the binding energy 284.80 eV) and carbonate (carbonate at the binding energy 288.5 eV). We can obtain the surface atomic concentration ratio of carbonate/ carbon which is 0.153 in table 2.

There is a difference observed after carbonation reaction by XPS analysis. The result was showed in Fig.A3. The carbonated one has one more chemical state than the other two in the surface that has the BE at 286.98 eV. By the handbook of XPS, the peak shift 287 eV can be considered as C-Cl, C-N , ether or another. The most possible is ether. Because it´s impossible that the sample contains the element Cl o N and contaminated by these gases. Ether is the most possible chemical state in the carbonated sample. The value of the surface atomic concentration ratio of Carbonate/Carbon is 0.179.

C 1s	Name	Position	FWHM	L.Sh.	Area	Area %	Ratio(Carbonate/Carbon)
Prepared	C 1s	284.80	2.925	GL(30)	8669.1	86.42	0.157
	C 1s	288.70	2.971	GL(30)	1364.7	13.58	
Cleaned	C 1s	284.80	2.81	GL(30)	8209.3	86.74	0.153
	C 1s	288.57	3.046	GL(30)	1254.4	13.26	
Carbonate	C 1s	284.82	2.364	GL(30)	10580.8	78.69	0.179

d	C 1s	289.27	2.641	GL(30)	1893.2	14.09
	C 1s	286.98	1.728	GL(30)	970.9	7.22

Table 2 A summary of the basic data of C1s spectra (Pyroxene) at 1 bar

Figure17 shows a comparison of high resolution survey-scans of C1s peak of sample Pyroxene during carbonation process. The binding energies of the C 1s peak for these three situations of the sample are approximately 284.80eV and the other nearly 289 eV. The carbonated one has one more state .The binding energy of the new chemical state is 286.98 eV. The shift peak of the new one is consistent with the BE value of ether.
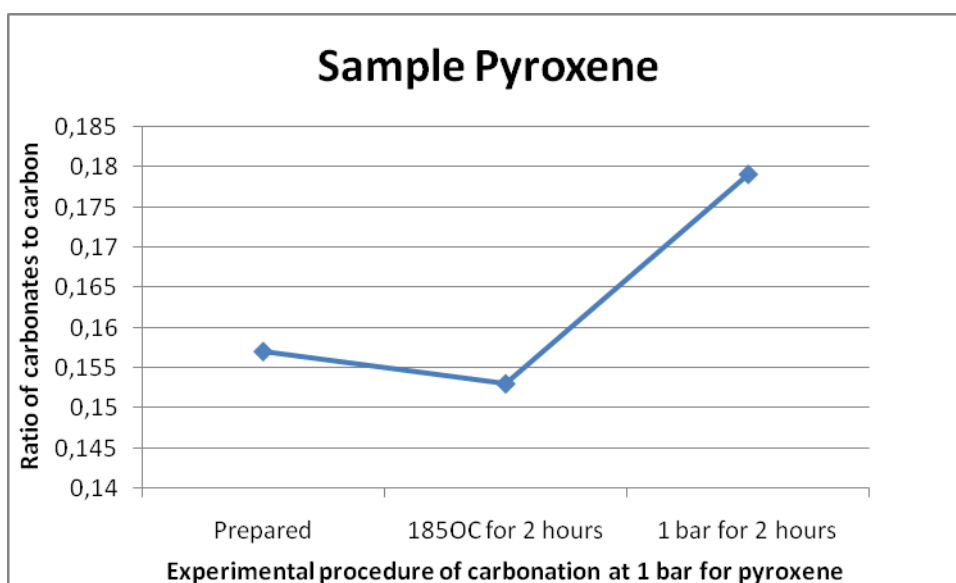

Figure 18 Ratio of CO_3^{2-}/C during experimental procedure at 1 bar (Pyroxene)

For the quantification analysis, XPS give relative concentration of elements in the surface of materials. Chemical states of carbon could be confirmed by the binding energy in the spectrum of C 1s. The surface atomic concentration of Carbonate/Carbon is different for each one during the whole reaction. The value of prepared one is 0.157, heated one is 0.153 and carbonated is 0.179. After the heating treatment, ratio of carbonates to carbon of Pyroxene reduced 2.5%. That suggests that heating Pyroxene could leach carbonates from the surface. After carbonation reaction at 1 bar four 2 hours, the ratio increased 17% compared to heated one. It means with injecting the flow of CO2, the surface becomes enriched in carbonate to carbon than the heated

sample. Figure 18 shows a comparison of carbonate relative to carbon at the surface of the Pyroxene during the reaction.

5.1.2 Sample Dunite

A low resolution survey scan of sample Dunite is shown in Figure 19. The energy peaks were observed in the survey scan and identified the elemental composition including C, O, Si, Ca, Fe, Mg that is shown in the Fig.19.
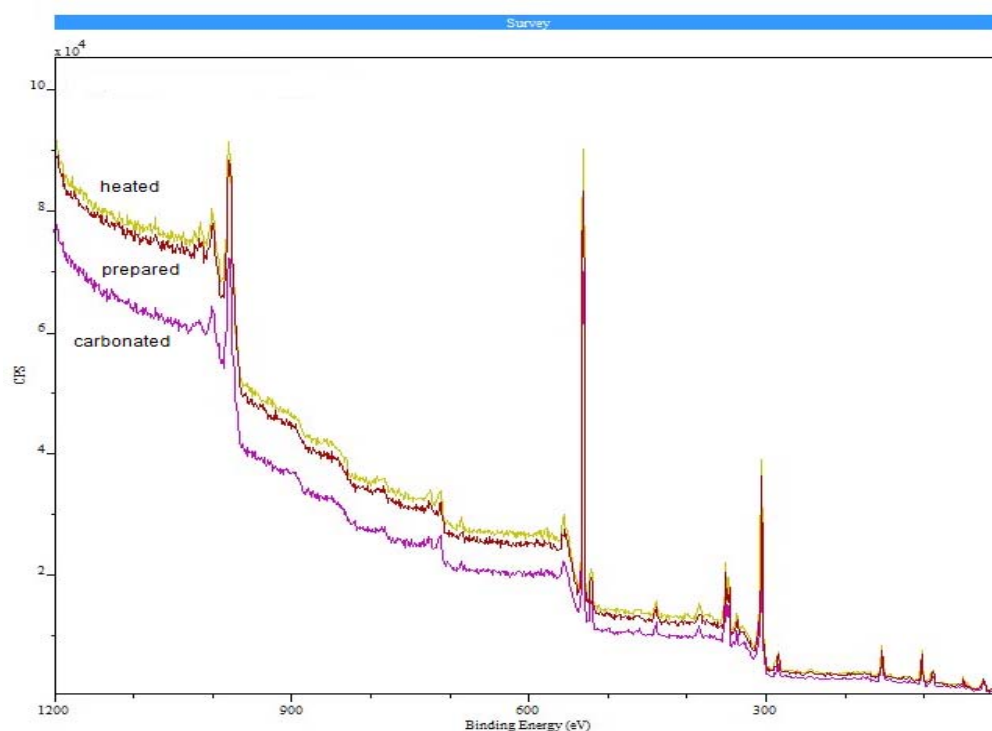

Figure 19 XPS survey scan of Dunite carbonation at 1 bar

We did the carbonation experiment for Dunite as the same as the Pyroxene. The goal of carbonation was obtained by two steps. First temperature was increased in $185^{O}C$ by heating treatment for 2 hours. And then injection CO2 reacted with the sample at 1 bar for 2 hours in the HPC of XPS. We checked the sample 3 times containing prepared one (before the heating treatment), cleaned one (after the heating treatment) and the carbonated one (before the carbonation procedure).

The C 1s binding energy average for carbonate is 289.3+/-0.6 eV. The binding energy of Carbon is 285 +/- 0.2 eV. The element of C of prepared Dunite in different states such as Carbon, Carbonate and ether (we have analysed above) has slightly different

characteristic binding energy. The information is obtained by the high resolution scans of the C1s peak which is showed in Fig.B1. On the other hand, for quantitative analysis we can acquire the Carbonate/Carbon ratio 0.248. We can find the ratio of Dunite is higher than the Pyroxene because of dolomite pre-existed in Dunite.

The C1s peaks of XPS after the heating treatment shown in Fig.B2 were qualitatively the same as the prepared one. It has just la little difference in the relative intensities of the three chemical state of C. The relative atomic concentration of carbon (at 284.82 eV) is 62.32%, carbonated is 14.23% (at 289.32 eV) , the other ether is 23.45% (at 286.45). The surface atomic concentration ratio of carbonate/carbon is 0.228 which is calculated with the data shown in Table 3.

The carbonated Dunite has three different chemical states at the surface of the material. They are carbon, carbonate and ether which are shown in the Fig.B3 and the data is presented in the Table 3. The ratio of carbonate/carbon is 0.260 that is obtained by the data from Table 3.
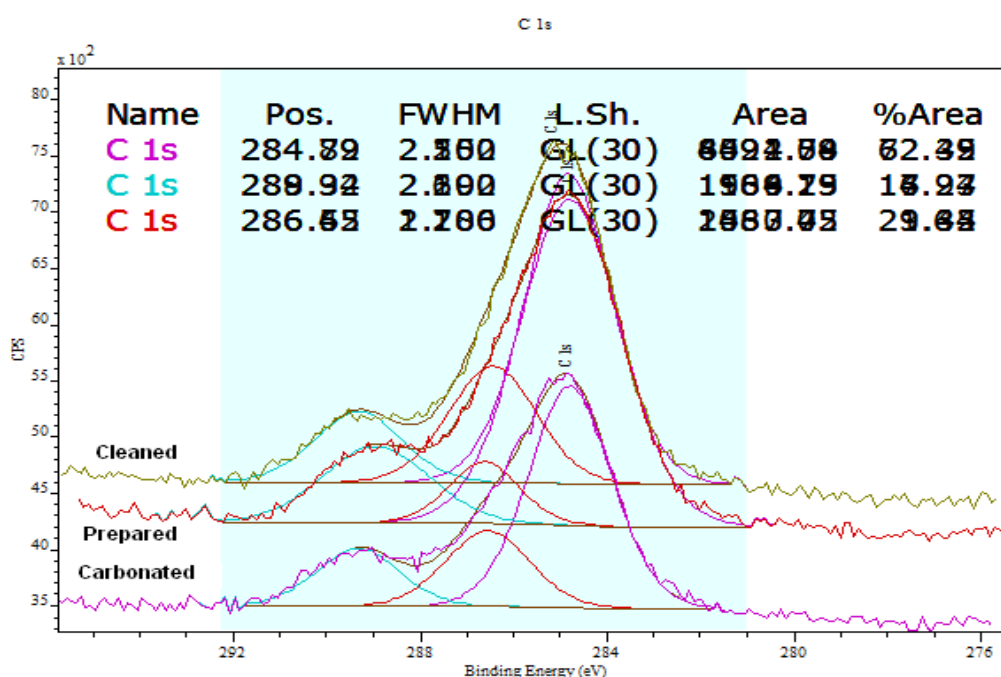

Figure 20 A comparison of XPS analysis for Dunite at 1 bar. The C1s peak is indicated.

C 1s	Name	Position	FWHM	L.Sh.	Area	Area%	Ratio carbonate/carbon
prepared	C1s	284.79	2.552	GL(30)	8022.09	72.39	
	C1s	288.94	2.692	GL(30)	1989.25	17.97	0.248
	C1s	286.62	1.786	GL(30)	1067.72	9.64	
cleaned	C1s	284.82	2.2	GL(30)	6594.54	62.32	
	C1s	289.32	2.2	GL(30)	1504.19	14.23	0.228
	C1s	286.45	2.2	GL(30)	2480.45	23.45	
carbonated	C1s	284.79	2.1	GL(30)	4491.78	62.45	
	C1s	289.32	2.1	GL(30)	1166.73	16.24	0.260
	C1s	286.55	2.1	GL(30)	1533.05	21.32	

Table 3 A summary of the basic data of 1 C1s spectra at 1 bar (Dunite)

The C 1s peaks of XPS of the sample Dunite during the experiment, shown in Fig.20, are quite the same, just a litter difference in the atomic concentration of the surface. The atomic concentration is presented by the area under the peak. In addition, there is difference in the ratio of carbonate/carbon which is shown in table 3.The salient feature of the experimental process indicate that when the heat treatment causes an obvious reduction in the ratio of carbonate/carbon. That means the heat treatment preferentially leaches carbonate from the surface.
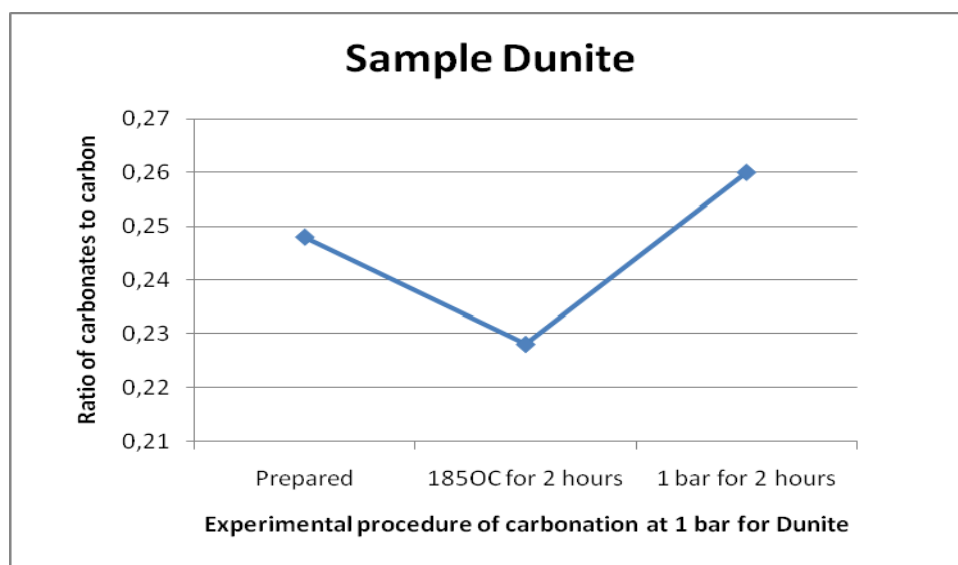

Figure 21 Ratio of CO_3^{2-}/C during experimental procedure at 1 bar (Dunite)

And then after the carbonation process, we can find out that the ratio increases from 0.288 to 0.260 (increasing 10.78%). In other words the heated sample (0.228) shows a lower ratio of carbonate/carbon than the prepared sample (untreated sample)(0.248), consistent with the removal of carbonate at the surface. After carbonation process, the carbonated sample shows a higher ratio (0.260) than the others, indicating a certainly addition of carbonate to the layer at the surface.

5.2 Temperature at 185°C(483K) and Pressure at 5 bar

5.2.1 Pyroxene

Fig.22 shows a comparison of XPS survey scan for pyroxene over a large energy at low resolution during the carbonation procedure at 5 bars, which presented O1s, Si2p, Mg2s, Ca2p, Fe2p and C1s peaks. XPS survey scans during the experiment were qualitatively the same, although subtle different in the relative intensities of each element.
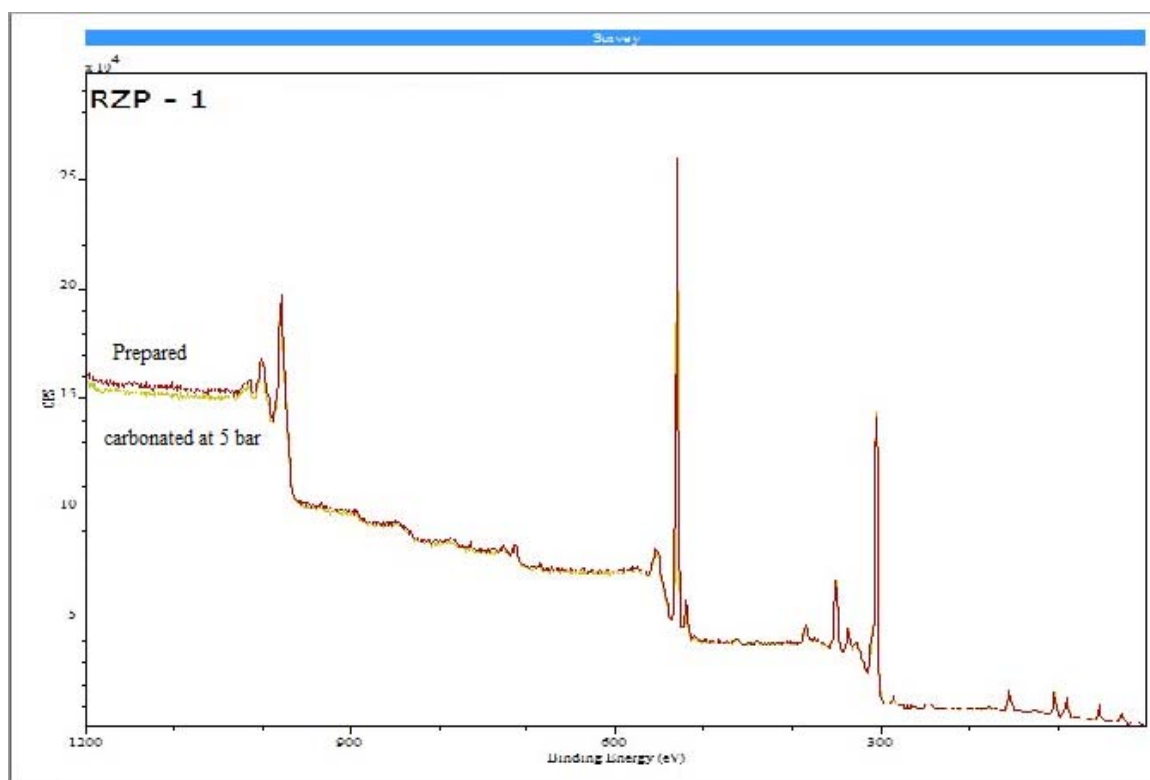

Figure 22 XPS survey scan for the Pyroxene carbonation at 5 bars

Representative high resolution XPS results for the C1s peak during the carbonation procedure are shown in Fig.23.The broad peaks suggest that a distribution of chemical state is presented. The band´s scope of C1s spectra for pyroxene before the carbonation experiment is from 280.46eV to 292.47eV. In the C1s spectra for the prepared pyroxene before the carbonation four chemical states are shown by observation of XPS. The binding energies of four chemical states are respectively 285.48eV, 283.44eV, 290.06eV and 287.06eV. We are really sure that chemical state of binding energy at 290.06 eV is carbonates and at 285.48 eV is carbon. Although we don´t quietly make sure the others, one could be considered as carboxyls (at 287.06eV).

Before heating the sample pyroxene and carbonation at 5 bars for 2 hours, high resolution XPS results for C1s peak is shown in the same Figure (Fig.A4). The binding energy of C1s peak for before and after carbonation experiment is approximately same. The C1s peak shifts to a higher binding energy of 289.52 eV whose chemical state is considered as carbonates. XPS confirmed the present of carbon at 285eV, so the chemical state at 284.64 considered as carbon in our case. We can obtain the ratio of carbonates to carbon which is 0.295 before the carbonation and 0.326 after the carbonation. Upon carbonation at 5 bars, the surface becomes enriched in carbonated relative to carbon (shown in A5).
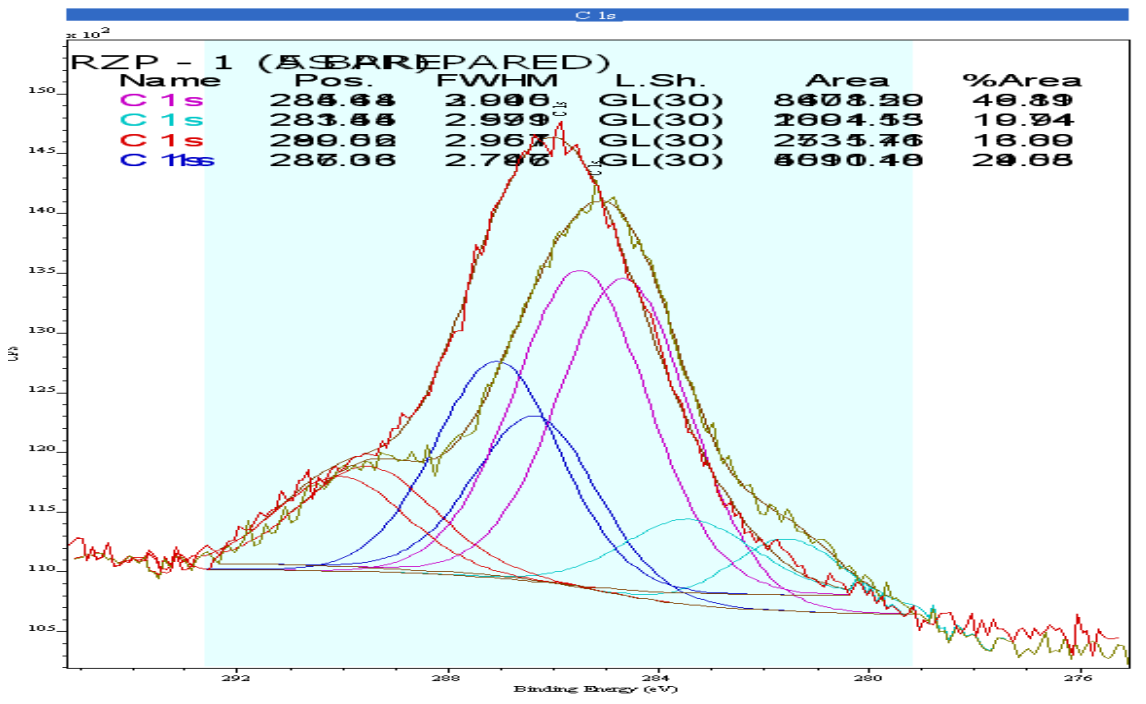

Figure 23 The C1s peak for the pyroxene carbonation at 5 bar for 2 hours

Pyroxene	Name	Position	FWHM	L.Sh.	Area	Area%	Ratio CO_3^{2+}/carbon	Growth rate
	C1s	285.476	3	GL(30)	8601.2	46.11		
	C1s	283.439	2.99	GL(30)	2004.6	10.74		
	C1s	290.058	2.95	GL(30)	2535.5	13.6	0.295	
Prepared	C1s	287.06	2.8	GL(30)	5510.4	29.55		
	C1s	284.64	2.95	GL(30)	8478.6	49.89		10.5%
	C1s	281.548	2.58	GL(30)	1691.1	9.94		
	C1s	289.52	2.97	GL(30)	2931.7	16.09	0.326	
Carbonated	C1s	286.333	2.74	GL(30)	4091.2	24.08		

Table 4 A summary of the basic data of 1 C1s spectra at 5 bars (Pyroxene)
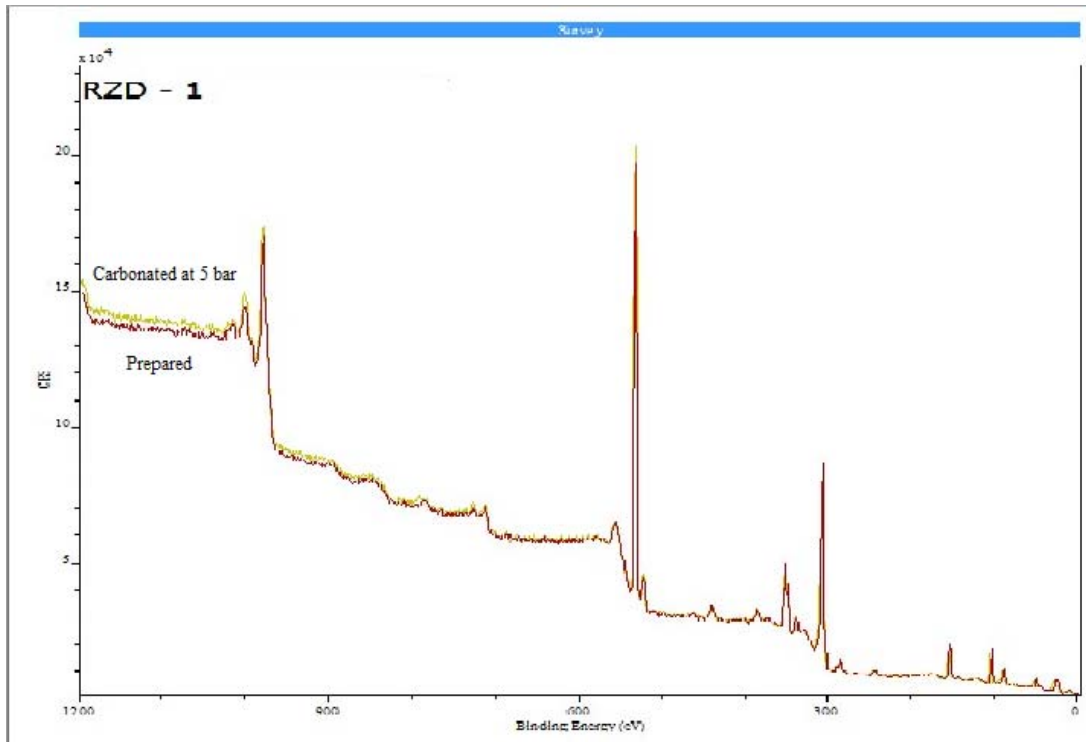
5.2.2 Dunite

Figure 24 XPS survey scan for the Dunite carbonation at 5 bars

For another sample Dunite, we did the same treatment to it. We checked the chemical compositions before the carbonation process as prepared sample and checked another time after the carbonation experiment at 5 bars with heating treatment for 2 hours by XPS. Representative low resolution survey scan of XPS results is shown in Fig.24.The energy peaks are observed by the survey scan and identified the elemental composition by the peaks of O1s, Si2p, Mg2s, Ca2p, Fe2p and C1s. There are differences of chemical states for Si 2s and C1s peaks. For the qualitative analysis of each element by XPS, almost all elements are the same between before carbonation reaction and after procedure except spectrum of Si 2s and C 1s.

For peak of Si 2s there are two chemical compositions at 153.42eV and 155.48eV after carbonation more than one chemical state of prepared one at 153.13eV. The Si 2s binding energy is relatively invariant with chemical state, so chemical change can be difficult to detect. In our experiment, we focus on the change of the ratio of carbonates to carbon at the moment before and after carbonation reaction.
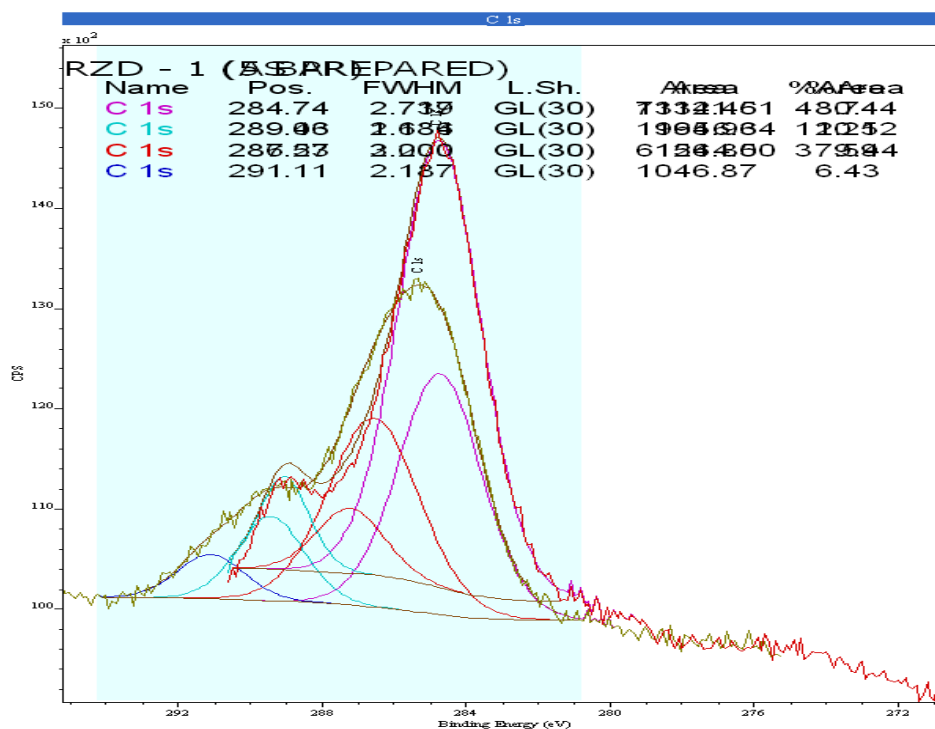
Figure 25 The C1s peak for the Dunite carbonation at 5 bars for 2 hours

Representative high resolution XPS result for the C 1s peak for the moment before and after carbonation reaction in XPS for 2 hours at 5 bars is presented in Figure 25. The binding energy of chemical state presented before the carbonation is BE at 284.74 eV, 289.06 eV and 287.23 eV. By the Handbook of XPS, we know the chemical state of BE at 284.74 eV is carbon the same as previous observation by XPS. The composition of BE at 289.06 is considered as carbonates in our experiment. Another with BE at 287.23 eV is possibly carboxyl via analysis of theory.

After the carbonation reaction at 5 bars for 2 hours, there is one more chemical state added by observation of XPS which is at 291.11 eV. Chemical change can be difficult to detect.

Dunite	Name	Position	FWHM	L.Sh.	Area	Area%	Ratio carbonated/carbon	Growth rate
Prepared	C1s	284.736	2.72	GL(30)	13141.5	80.44	0.126	122%
	C1s	289.065	1.63	GL(30)	1656.3	10.12		
	C1s	287.232	2.2	GL(30)	1544	9.44		
Carbonated	C1s	284.738	2.738	GL(30)	7132.5	43.74	0.280	
	C1s	289.434	2.186	GL(30)	1995	12.25		
	C1s	286.57	3	GL(30)	6126.9	37.59		
	C1s	291.11	2.187	GL(30)	1046.9	6.43		

Table 5 A summary of the basic data of 1 C1s spectra at 5 bars (Dunite)

At last, we look at the ratio of carbonates to carbon in the sample Dunite at 5 bars with heating treatment at 185^OC for 2 hours. The table 5 shows the ratio, before the reaction it is 0.126 and after reaction it is 0.280. The growth rate of the ratio after carbonation reaction at 5 bars is one more time than before the carbonation reaction. We can observer obvious change of carbonates produced during carbonation procedure by this data.

Chapter 6

Conclusion

In situ gas-solid carbonation reaction betwween powdered Pyroxene and Dunite in solid and CO_2 gas was investigated to determine the feasibility of converting carbon dioxide in the atmospheric to a stable form carbonates such as calicite or magnesite. Amounts of previous experimens were done by using water-dissolution or acid treatment to dissolve the sample at the first, but for our experiment we didn´t do anything before the carbonation reaction expect powder the samples and heating them at $185^{\circ}C$ which is optimized temperature for our experiment.

The carbonates exisited at the surface of the samples was removed using heating treatment (presented in Figure 18-21)

The components of Pyroxene and Dunite were observed by XRD at ambient temperature($24-25OC$). Pyroxene and Dunite was characterized using XPS before and after treatment including heating treatment and carbonating treatment at various pressure conditions. The carbonation procedure was produced in HPC of XPS without the contamination. XRD checked the components of the samples in the deplt and XPS just examined the surface of the samples.
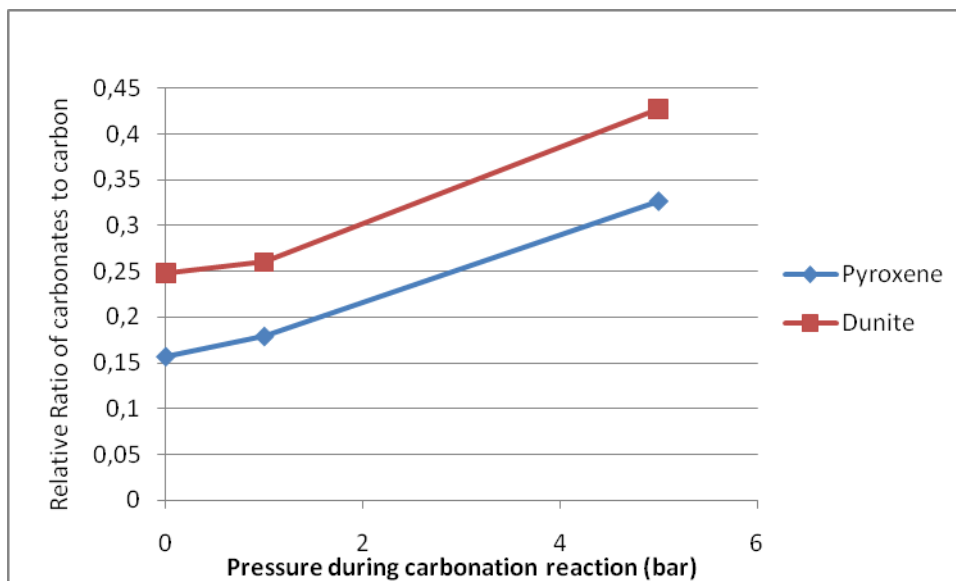

Figure 26 Relative ratio of carbonates to carbon at 1 bar and 5 bars

The XRD data shows that the components of the two different samples are similar(shown in Table 1) . There is a little difference in components of two samples.

We find out that there is dolomite pre-existing at the beginning in the Dunite, but is doesn´t be found in the Pyroxene.

In addition by XPS analisis the trend of the carbonates to carbon of two different samples are similar too(shown in Figure 26). Two lines have the similar trend that the rate of carbonate preduced is increasing with rising the pressure, although carbonation reacts in solid-gas without dissolution treatment.

At the beginning of the observation about ratio of carbonates to carbon, figure 26 shows Dunite´s ratio is greater than the Pyroxene´s because of dolomite pre-existing in Dunite.

The growth rate of the ratio(CO_3^{2-} /C) of Dunite at 5 bars compared to 1 bar is quite high. The value is 122%. The value of Pyroxene just is 10.5%(shown in Table 4-5)

The potential for in situ carbonation(gas-solid) in ultramafic rock observed that carbonation rate is increasing with pressure increase at optimized temperature($185^{o}C$).

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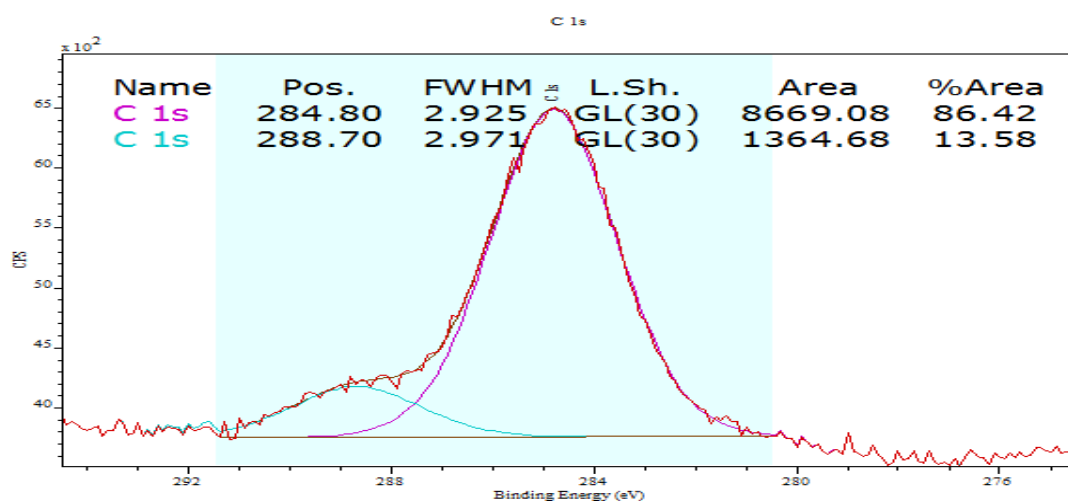# Appendix A – C 1s peak for Pyroxene(1bar,5bars)

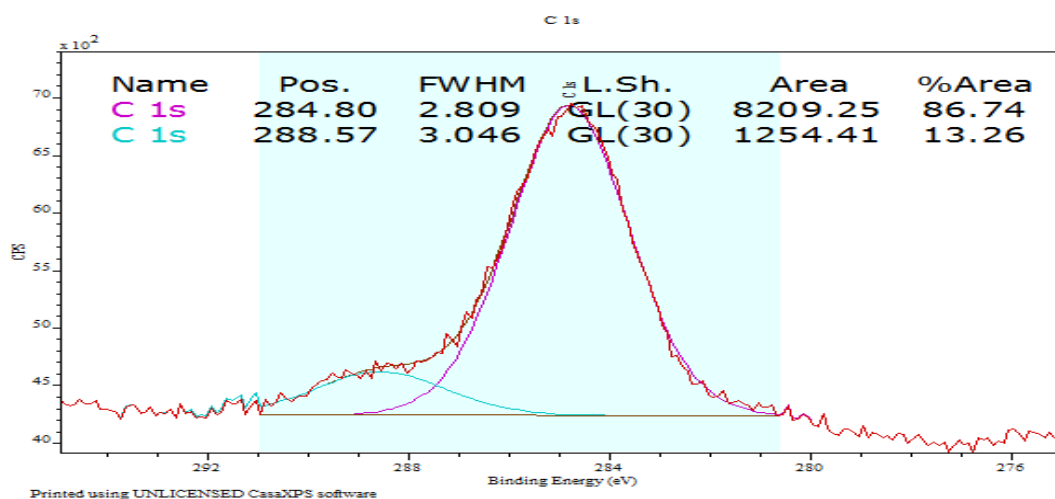Figure A1 The C1s peak for the Prepared Pyroxene of carbonation reaction (untreated)

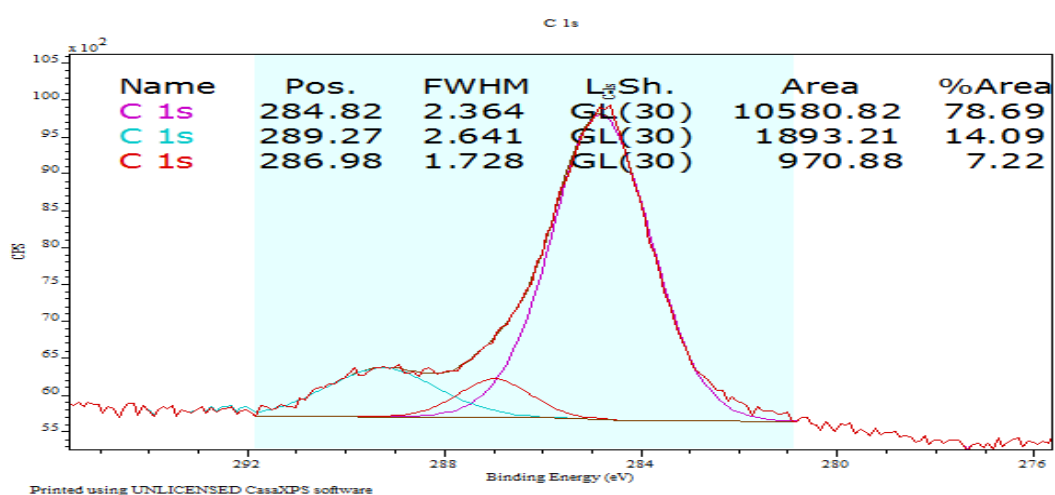Figure A2 The C1s peak for the Prepared Pyroxene of carbonation reaction at 185°C

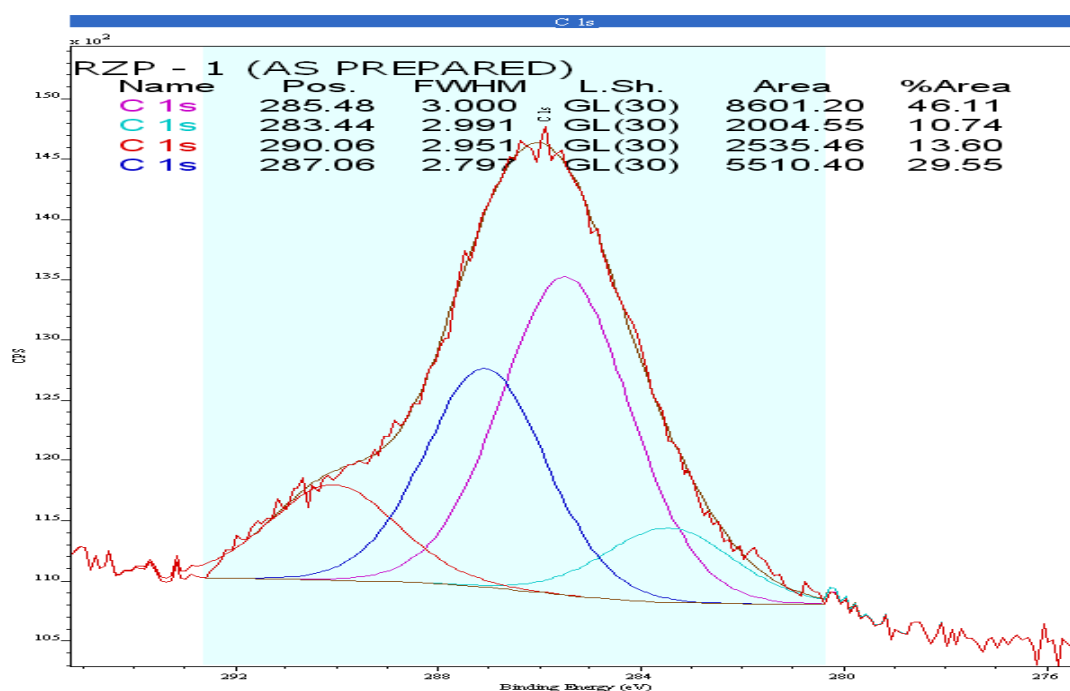**Figure A3 The C1s peak for the Prepared Pyroxene of carbonation reaction at 1 bar and ambient temperature**

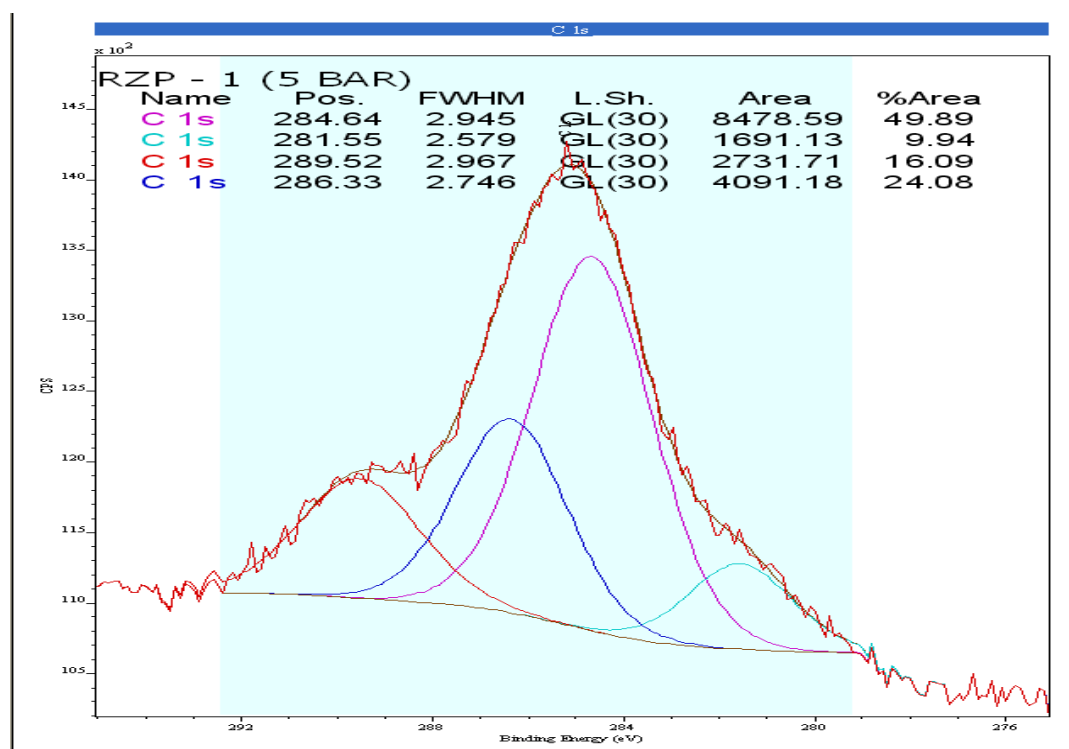**Figure A4 The C1s peak for the Prepared Pyroxene at ambient temperature**

Figure A5 The C1s peak for the Pyroxene of carbonation reaction at 185°C and at 5 bars.
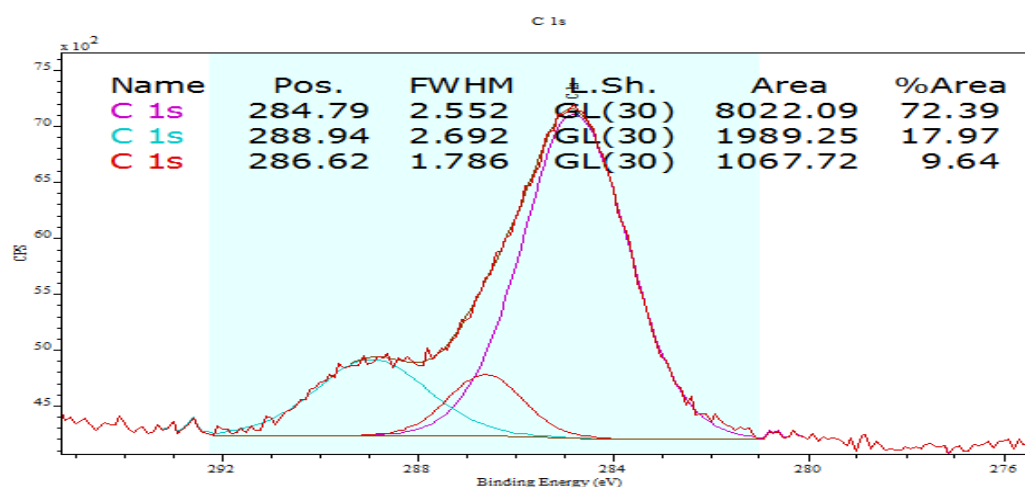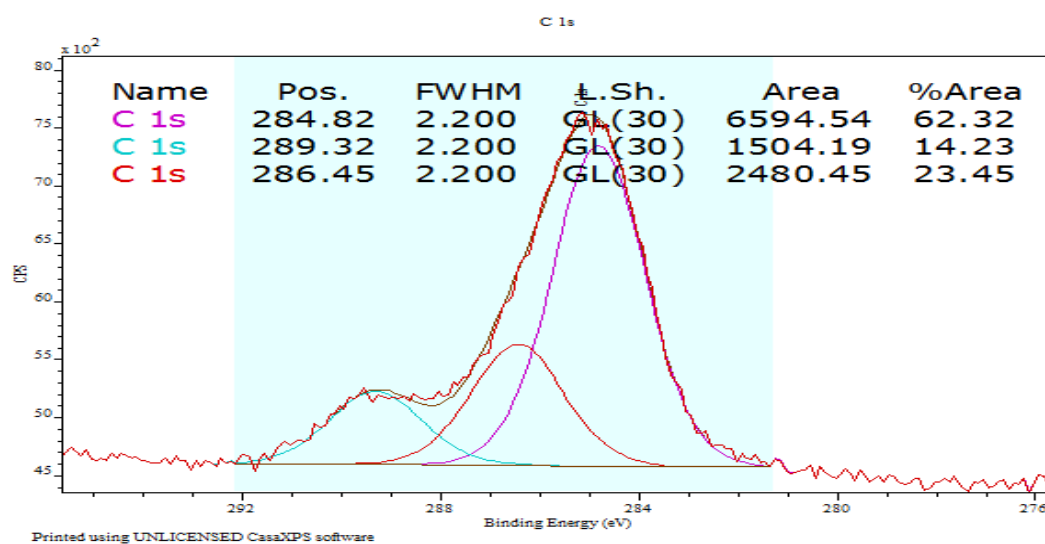
Appendix B- C 1s peak for Dunite(1bar,5bars)

C 1s

x 10²

Name	Pos.	FWHM	L.Sh.	Area	%Area
C 1s	284.79	2.552	GL(30)	8022.09	72.39
C 1s	288.94	2.692	GL(30)	1989.25	17.97
C 1s	286.62	1.786	GL(30)	1067.72	9.64

Binding Energy (eV)

Figure B1 The C1s peak for the prepared Dunite of carbonation reaction (untreated)

C 1s

x 10²

Name	Pos.	FWHM	L.Sh.	Area	%Area
C 1s	284.82	2.200	GL(30)	6594.54	62.32
C 1s	289.32	2.200	GL(30)	1504.19	14.23
C 1s	286.45	2.200	GL(30)	2480.45	23.45

Binding Energy (eV)

FigureB2 The C1s peak for the heated Dunite of carbonation reaction at 185°C

C 1s

x 10²

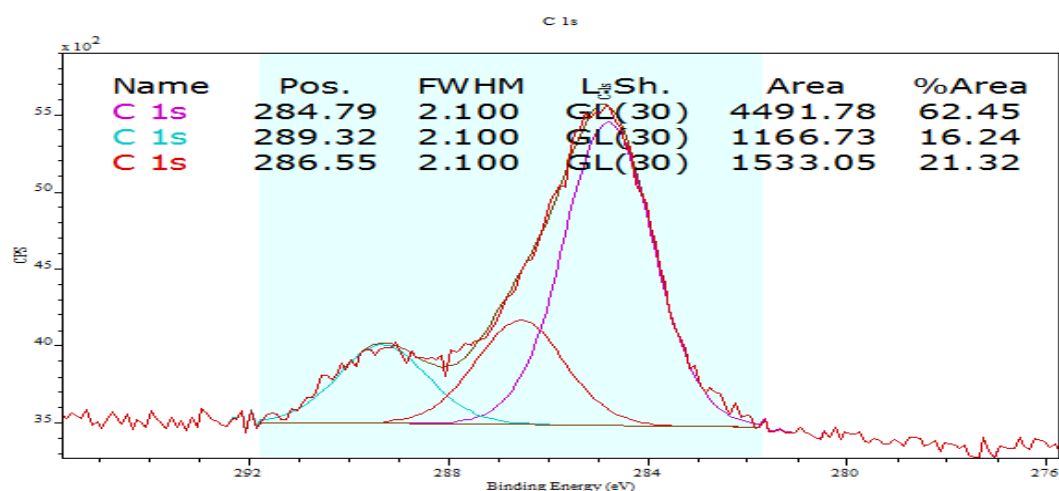| Name	Pos.	FWHM	L.Sh.	Area	%Area
C 1s	284.79	2.100	GL(30)	4491.78	62.45
C 1s	289.32	2.100	GL(30)	1166.73	16.24
C 1s	286.55	2.100	GL(30)	1533.05	21.32

Binding Energy (eV)

Figure B3 The C1s peak for the carbonated Dunite of carbonation reaction at 1 bar
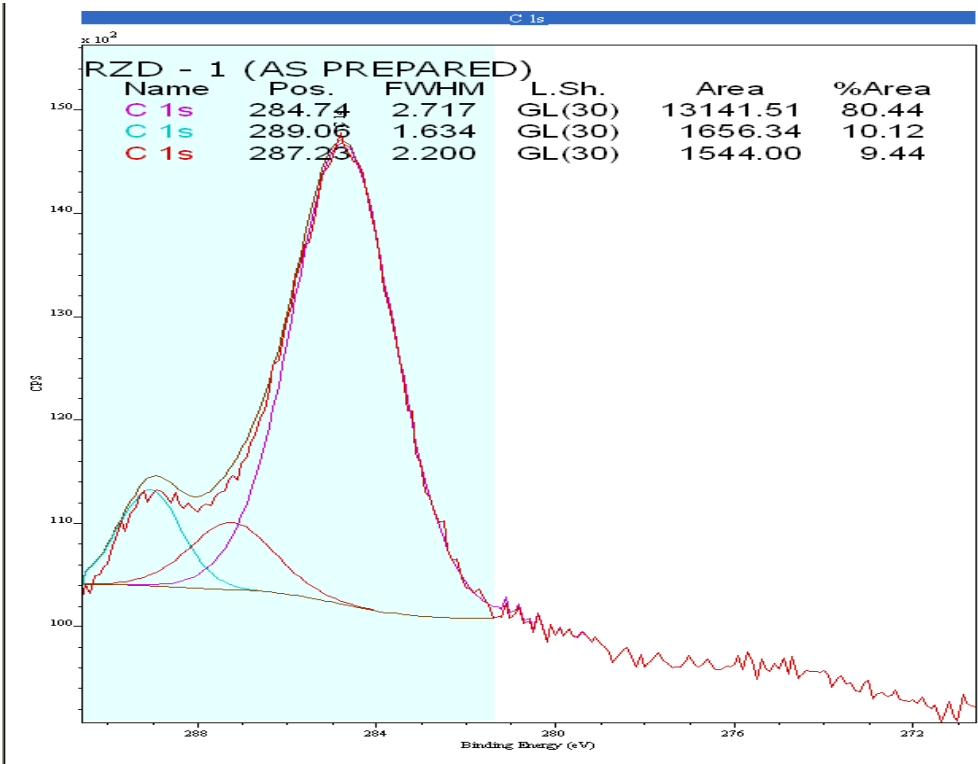

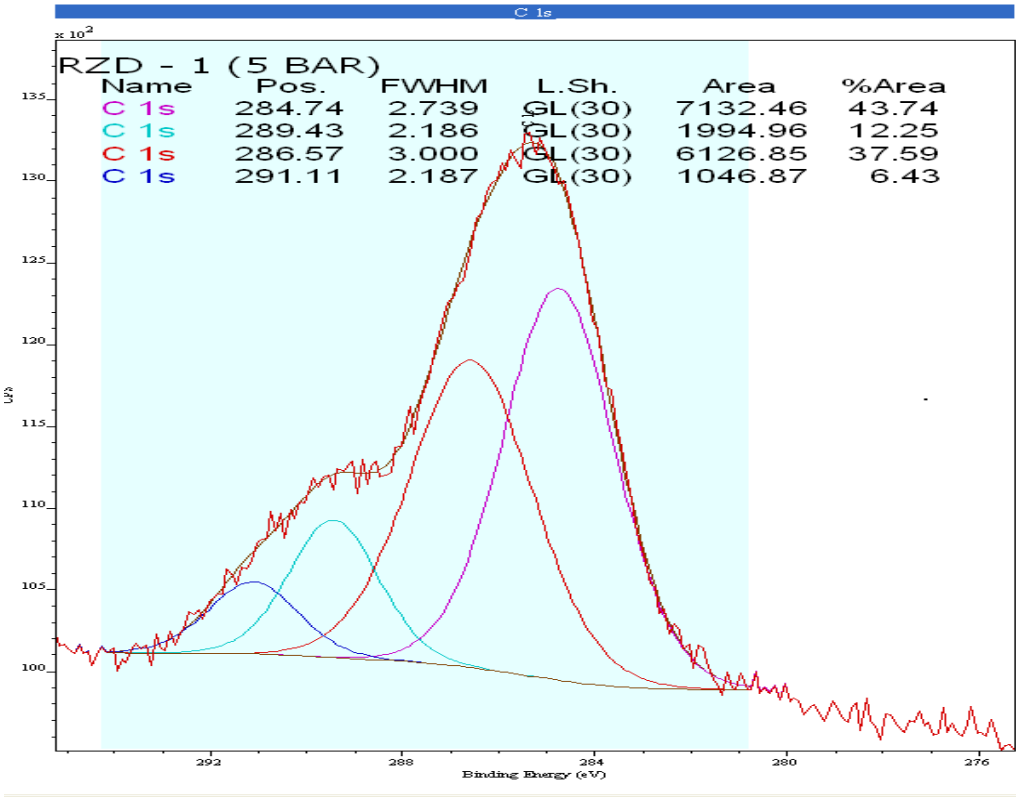**Figure B4 The C1s peak for the Prepared Dunite at ambient temperature**

Figure B5 The C1s peak for the carbonation reaction of Dunite at 5 bars.