



Contrasted Speciation of Iron in Obsidians and Tektites: a Spectroscopic Study

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"The first gulp from the glass of natural sciences will turn you into an atheist, but at the bottom of the glass God is waiting for you."

– Werner Heisenberg

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~to make a **bad day** worse, spend it **wishing** for the **impossible**~



Abstract

Obsidian and tektite are aluminosilicate glasses bearing Fe formed through geological phenomena. Obsidians are formed during volcanic events whereas tektites are associated with rock fusion during giant extraterrestrial impacts on Earth followed by fast cooling during ejection of molten material.

Because Fe plays an important role in determining the physical properties and coloration of glasses, we focused our study on the speciation of Fe in obsidian and tektite glasses using optical absorption spectroscopy (OAS). Spectra are recorded between 25°C and 600°C using a new device allowing to measure the optical absorption spectra of glasses through a furnace. Complementary data on Fe^{3+} in tektites have been obtained using electron paramagnetic resonance (EPR).

In tektites, we show that Fe^{2+} is incorporated in the glassy structure in tetrahedral and five-fold coordinated sites. Fe³⁺ is barely visible in OAS. Nevertheless, EPR confirms the presence of Fe³⁺, at low concentrations, showing that Fe is mostly reduced in these glasses. Thus, spectroscopic data indicate that iron speciation in tektites retains the memory of the blow up of the surrounding atmosphere during the giant meteoritic impact.

In obsidians, OAS reveals a major contribution of Fe^{2+} absorption bands, indicating a regular octahedral site, an unusual environment compared to tektites and synthetic glasses. The presence of Fe-oxide nano-clusters, suspected since a long time from previous EPR studies, is confirmed by variable-temperature OAS in all the obsidians that were analysed. Complementing previous data on low temperature OAS, our data at high temperature show a specific absorption bands, assigned to Fe-Fe and Fe-Ti intervalence charge transfers (IVCT), which is characterised by a spectacular intensity dependence as a function of temperature over 1,000 K (10 K – 1,000K). This thermallyactivated behaviour shows an activation energy similar to that observed for IVCT in various minerals. The evidence of specific Fe²⁺ sites and of IVCT processes show the presence of Fe-oxide clusters. By contrast, tektites do not show such contributions. These clusters, showing a local re-arrangement around Fe, are related to the cooling history of the glass, as they are not found in the medium range structure of synthetic glasses. The existence of these clusters and their nature seem to be related to the conditions of formation of the obsidians that were studied. Moreover, they explain the dark appearance of obsidians compared to the light green tektites.

Résumé

Les verres d'obsidienne et de tectite étudiés sont des verres alumino-silicatés formés par des processus géologiques. Les obsidiennes sont formées lors d'éruptions volcaniques alors que la formation des tectites est associée à de gigantesques impacts météoritiques au cours desquels la fusion des roches encaissantes associée au choc est suivie d'un refroidissement rapide du matériel en fusion éjecté dans l'atmosphère.

Le Fe jouant un rôle majeur dans les propriétés physiques et la coloration des verres, nous avons centré notre étude sur sa spéciation dans des verres d'obsidienne et de tectite par spectrométrie d'absorption « ultraviolet-visibleproche infrarouge » (OAS). Des spectres ont été mesurés à des températures allant de 25 °C à 600 °C, en utilisant un nouveau montage permettant de mesurer le spectre d'absorption d'un verre situé dans un four. La résonance paramagnétique électronique (RPE) a permis d'obtenir des données complémentaires sur le Fe³⁺ dans les tectites. Les résultats obtenus sur les tectites montrent que le Fe²⁺ est incorporé dans la matrice vitreuse en coordinations quatre et cinq. Le Fe³⁺ est difficilement détectable par OAS. Les résultats en RPE confirment sa présence, en faible concentration, démontrant que le fer est principalement ferrique dans ces verres. Ainsi, les données spectroscopiques montrent que la spéciation du fer dans les tectites garde en mémoire l'absence d'oxygène dans l'atmosphère lors de leur formation, celle-ci ayant été soufflée par le gigantesque impact météoritique.

Dans les obsidiennes, l'OAS révèle une contribution majeure de la bande d'absorption du Fe^{2+} , indiquant un environnment octaédrique régulier, inhabituel lorqu'on le compare à celui des tectites ou des verres synthétiques. Le regroupement des cations du Fe à nano-échelle (« *clusters* »), déjà suspecté du fait d'études en RPE est confirmé par la OAS à haute température (jusqu'à 600°C) dans toutes les obsidiennes analysées. Après une étude précédente en OAS à basse température, nos données à haute température montrent la présence d'une bande d'absorption spécifique, associée à un transfert de charge d'intervalence (IVCT) Fe-Fe ou Fe-Ti, mise en évidence du fait de la spectaculaire diminution de son intensité lorsque la température augmente, entre 10 K et 1000 K. Les preuves de la présence de Fe²⁺ dans des sites spécifiques, ainsi que les processus d'IVCT indiqueraient la présence de « *clusters* » d'oxydes de fer. *A contrario*, les tectites étudiées ne présentent pas ce comportement. Ces « *clusters* », montrant un réarrangement local autour du fer, sont liés à l'histoire thermique du verre car ils sont absents de la structure à moyenne distance des verres synthétiques et des tectites. L'existence de ces « *clusters* » et leur nature semblent être liés aux conditions de formation des obsidiennes étudiées. De plus, ils expliquent l'aspect noir sombre des obsidiennes comparé aux tectites vertes et translucides.

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Introduction

Most natural silicate glasses are formed through geological phenomena, with the noticeable exception of amorphous biogenic silica in diatoms. Among them, obsidians and tektites are of great interest. Obsidians are aluminosilicate glasses bearing iron and alkali formed during rare volcanic events, such as in subduction contexts (American Cordilleras, Japan...) and in the Mediterranean basin. The progressive cooling of a highly viscous melt during the ascent in the continental crust and the final quench at the contact with the atmosphere forms a massive vitreous material. The formation of tektites, also iron-bearing aluminosilicate glasses, containing alkaline and alkaline-earths (in contrast with obsidians), is associated with giant extraterrestrial impacts on Earth leading to fusion and mixing of the impacted rocks and the meteorite. This is followed by fast cooling during ejection of molten material in strewn fields over thousands of km (e.g., Central Europe, North America...).

Many fields are concerned by these natural glasses. As they were used as tools or jewellery by many human civilisations since about 10,000 years, the chemical characterisation of these glasses is currently used by archaeologists to determine their sources and reconstruct prehistoric trade or exchange relationships and group mobility pattern through ancient times (Hughes and Smith, 1993). Furthermore, Earth scientists have also long been fascinated by these materials. Obsidians are unique evidence of eruption processes because they represent a frozen picture of magmatic melts. Therefore, oxidation state of iron in obsidians and obsidians thermal history have been widely studied, e.g. Leonhardt et al. (2006); Newman et al. (1988). Tektites may also keep the memory of catastrophic asteroid impacts during geological history and redox conditions have been questioned in these glasses to better understand their formation process (Giuli et al., 2002). In materials and glass sciences, the longevity of such natural glasses, which can be millions of years old, demonstrates that glasses may be preserved in geologic environments and can be considered as good analogues for modeling some processes that may appear during the geological storage of nuclear glasses (Ewing, 1979).

Intriguing by many aspects, these materials also have striking and distinct visual properties, despite having similar iron content. Both tektites and obsidians are transparent glasses, but obsidians are deep black to brown whereas tektites are lighter and close to the green colour of most technological glasses containing iron (figure 1, a, b and c). This observation may be linked with their contrasted thermal history presenting contrasting cooling rates compared to industrial glasses. The large volume of magmatic liquids (of the order of km³) imposes cooling during years after the eruption (figure 1, d) and extremely slow cooling rates for obsidians. By opposition, hyperquenching occurs when low amounts of melt are ejected and quenched in the atmosphere to form a tektite. As shown by the studies cited above (Newman et al., 1988; Giuli et al., 2002), iron, through redox and speciation, is a probe to determine the conditions of formation and thermal history of these glasses. As colour results from the absorption of light by iron, our study focused on the origin of colour differences between tektites and obsidians. The objective was to give insight into iron speciation and, by this way, glass thermal history and glass ageing.

Thus, during this master thesis, optical absorption spectroscopy (OAS) was used in transmission on selected obsidian and tektite glasses. Indeed, this method reveals absorption bands in the ultraviolet (UV)-visible-near infrared (IR) range due to optical absorption by electronic transitions in transition elements, such as iron. Moreover, low temperature studies (between 10 K and room temperature) had already given interesting and surprising results on Fe speciation in obsidians (Galoisy et al., in prep.). In order to get additional information, we realized the first *in situ* high temperature optical absorption measurements on geological glasses. Electron paramagnetic resonance (EPR) has been used as a complementary method to get information on ferric iron in tektites.



Figure 1: Photographs of: (a) an obsidian sample from the Mono Craters (California, USA), (b) a tektite sample from Bohemia (Czech Republic), (c) a synthetic sample of Fe bearing soda-lime glass, (d) the Panum Crater volcano from the Mono Craters (California, USA), the volcanic dome, which last erupted in 1,325 A.D., is about 1,200 metres in diameter and is made of pure obsidian glass.

1 Geological and Physical Background

1.1 Natural Glasses Occurrence and Formation

A wide variety of natural glasses has been identified by geologists. They can be divided in two main types, if amorphous materials, which are not glasses *sensu stricto*, are excluded (e.g. amourphous silica of diatoms). The first and main type, volcanic glasses, results from aerial or submarine eruptions. These glasses are classified according to chemical composition, a parameter depending on the geological context of the volcanism and the evolution of the melt in the magmatic chamber of the volcano. Basalts, pumices and rhyolites are the most common glassy rocks, though they can hardly be considered as bulk monolithic glasses. Indeed, the rock structure is composed of numerous μ m-sized crystals and air vesicles, that account sometimes for less than 10% of the total volume. Some crystals can even reach a few mm. Thus, volcanic glasses are far from synthetic glasses. Only one, obsidian, has an extensive glassy matrix containing a few crystals at a mm scale (Ericson et al., 1975). The second type, impact glasses, is formed after a meteoritic impact by a giant bolide. The glasses formed can

stay around the area of impact and are called impactites. Some glasses, the tektites, can be found over thousands of kilometres around the crater. The structure of the former glass reveals the presence of fragments of rocks called clasts, resulting from the impact, dispersed in a glassy matrix. By contrast, tektite texture is homogeneous with only scarce air vesicles. Tektites have been chosen because they are considered as witnesses of some of the most important events suffered by our planet, such as the global extinction at the Cretaceous-Tertiary boundary (Smit et al., 1992). In addition, they present significant analogies with synthetic glasses.

The first natural glass studied, obsidian, is associated with the formation of a volcanic dome. This process begins with a slow melt ascent in a volcano vent because of the pressure in the volcanic chamber below. The arrival at the surface results in the progressive growth of a dome structure (figure 1, d and figure 1.1). Indeed, melt flow is prevented by the high viscosity of the melt. Then, the contact with the cool atmosphere leads to the slow cooling of the melt. Due to the large volume of molten materials, a few days to a few months are necessary (Gottsmann and Dingwell, 2001). Despite the slow cooling rate, the high viscosity of the melt leads to the formation of a glass. When the viscosity of the melt is lower, a slow lava flow takes place near the dome. Obsidian glass is formed at the surface of the flow (Bigazzi et al., 1992), as shown in figure 1.1. Sometimes, gas pressure under the dome is too high and the dome explodes leading to a catastrophic event called pyroclastic flow. Fragments of solid rocks, associated with hot gases and melts hurtle down the slope of the volcano forming some small round pieces of obsidian, often called marekanite.

These events take place near subducting plate geological context or at divergent plate boundaries. The former consists in the diving of an oceanic plate (as the Pacific plate) under a continental plate (as the North American plate). Thus, it explains the frequent occurrence of obsidians all along the Andes and the Rocky Mountains. The latter geological context is an area where two plates move away. This is the case in some parts of the Mediterranean basin.

The chemical composition of most natural obsidians is rather uniform because of similar formation processes. A range of standard obsidian compositions is given in table 1.1. They are characterised by a highly siliceous composition. The glass is almost completely dehydrated, with less than 1 wt% of water, due to the degassing of most of the water during the formation process. Among the transition elements likely to play a role in the colour of the glass, the main one is Fe. In addition, Ti and Mn, even at low concentrations, could also take part in the phenomenon.



Figure 1.1: Illustration of a volcanic dome (A) associated with a lava flow (B), in black: obsidian glasses, from Frahm (2012).

The conditions of formation of tektites, the second glass studied during this master placement, has long been debated. Nowadays, it is commonly accepted that they formed after rare and particularly extreme impacts of giant meteorites (Dressler and Reimold, 2001). Upon impact, a part of the kinetic energy is converted in thermal energy, provoking vaporization and fusion of the material impacted. In gigantic events, the melt formed can be ejected over hundreds to thousands of km and is cooled extremely fast in the atmosphere (figure 1.2). The process forms these glass pieces, called tektites, of various shapes and sizes going from several μ m to tens of cm.

So far, only four strewn field have been discovered. Three have been associated with a specific crater impact. The crater, source of the strewn field in North America, is suggested to be the Chesapeake structure, near the east coast of United States while the tektites from Ivory Coast are linked to the Bosumtwi crater in Ghana. Tektites from Central Europe, also called moldavites, were ejected from the Ries impact crater in Germany. The australasian strewn field, where layered tektite, called Muong Nong-type have been discovered are thought to come from an undiscovered crater in Indochina (Dressler and Reimold, 2001).

Tektites chemistry reveals a highly silicic content, such as obsidian. A range of standard tektite compositions is given in table 1.1. Tektites have generally a low alkaline content and are enriched in alkaline-earth elements compared to obsidians. Moreover, they are completely dehydrated. The main transition element is still Fe.



Figure 1.2: Schematic drawing of a meteoritic impact: a) Approach of meteorite or comet. b) Impact, evaporation of projectile and fusion of the material impacted (black lines). c) Ejection of the melt. d) Shape of a strewn field, area of landing of the tektites.

	SiO_2	Al_2O_3	Na ₂ O	K_2O	MgO	CaO	TiO_2	MnO	FeO	$\mathrm{H}_{2}\mathrm{O}$
Obsidians ^a	70-80	10-15	3–5	4-6	0.01-0.1	0.2–0.8	0.01-0.1	0.01-0.1	0.5–2	0.1 - 1
$Tektites^{o}$	65 - 80	10 - 15	0.5 - 2	1 - 4	0.5 - 5	0.5 - 4	0.1 - 1	$0\!-\!0.1$	1 - 6	

Table 1.1: Standard range of chemical composition for obsidians and tektites (^{*a*}: compilation from McCall (2005), ^{*b*}: compilation from Dressler and Reimold (2001)).

1.2 The Glassy State

Beyond geological features, the spectroscopic properties of obsidians and tektites, are the aim of this study. They can be defined as silicate glasses, in the common physical meaning of the term. Indeed, they are amorphous solids presenting a glass transition (Zarzycki, 1991), i.e. a dramatic modification of the second order thermodynamic properties (heat capacity, c_p , and thermal expansion, α) from near liquid to near solid values.

The structure of silicates is complex and can be partially described by different models. It has been first schematically represented as a random three dimensional network in the Zachariasen model (Zachariasen, 1932). In this model, silicon tetrahedra (SiO₄) share corners forming a continuous random network. Thus, Si⁴⁺ is called a network-former. Alkaline or alkaline-earth ions, present in tektites and obsidians, have higher ionic radii and are characterized by ionic bonding to oxygen. These network modifiers creates non-bridging oxygens in the glassy network. This causes important modifications on the structure and physical properties of glasses. For instance, it decreases the glass transition temperature and the viscosity. These cations are called network-modifiers. In the glasses studied, Al^{3+} can be considered as a network forming cation. In spite of the charge deficiency induced by the formation of AlO₄ tetrahedra instead of SiO₄ tetrahedra, the presence of alkaline and alkaline-earth cations allows charge compensation essential to electroneutrality.

Most of Zachariasen rules are empirically verified but this model is very simple considering the progresses made in calculation and experiments on glasses. Many aspects of glass structure are still debated, such as the distribution of network-modifying cations in the network. This is why more complex models are given. The most important, the modified random network has been proposed by Greaves (1985). Glass structure is described as a covalent rigid network containing mainly network-forming cations associated with a network of channels containing the mobile alkaline and alkaline-earth cations (figure 1.3).



Figure 1.3: Illustration of the modified random network, from Greaves (1985) (small black circles: alkali, small white circles: silica, large white circles: oxygens).

1.3 Transition Elements in Glasses and Optical Absorption

1.3.1 Incorporation of Transition Elements in the Glass Network: the Case of Iron

Transition elements are particularly efficient colouring agents at the origin of colour in many materials. The colour of natural and industrial glasses is attributed to the incorporation of transition elements in the glass structure. Local environment and oxidation state are the most important parameters explaining the specific colour of a material bearing a transition metal. Thus, understanding the environment of transition elements in glasses is a key issue to determine the origin of colour.

Fe is the main transition element observable in tektites and obsidians and has long been studied in industrial glasses. Fe in glasses is generally a mixture of Fe^{2+} and Fe^{3+} which ratio depends on the oxidation of the environment during glass formation. In the most schematic picture of Fe-bearing glasses, Fe^{3+} is considered to be a networkforming cation, included in tetrahedra forming the network (Kurkjian and Sigety, 1968). In the other hand, Fe^{2+} is regarded as a network-modifying cation in octahedral coordination (Fox et al., 1982). Nevertheless, numerous parameters are involved in modifying the Fe environment, such as the chemical composition of the glass, the oxidation state or even the thermal history. Thus, the various spectroscopic method used on Fe-bearing glasses as Mössbauer spectroscopy (Rossano et al., 1999), X-ray absorption spectroscopy (Calas and Petiau, 1983), optical absorption spectroscopy (Bingham et al., 2007) or a combination of methods (Bingham et al., 2002) revealed the presence of 4, 5 and 6-fold coordinated Fe^{2+} and 4 and 6-fold coordinated Fe^{3+} . However, speciation is composition-dependent and, in addition, all studies are not in perfect agreement.

The mechanisms of colouring by Fe and other transition elements are well-described by crystal field theory which is doing the link between light absorption and transition element environment in glasses. Thus, the use of this theory to interpret optical absorption spectra could give insight into Fe environment in tektites and obsidians.

1.3.2 Crystal Field Theory and Optical Absorption

Crystal field theory describes the effects of the electrostatic field of anions or ligands on the orbital energy levels of a transition element. The surrounding ligands are considered as point negative charges (Burns, 1993). The Hamiltonian of a cation in a field of ligand is modified as follows:

$$\mathcal{H} = \mathcal{H}_{\mathcal{F}} + \mathcal{V},\tag{1.1}$$

where \mathcal{H} is the potential of the free ion and \mathcal{V} is the potential induced by the presence of the ligands. In the case of transition elements, the degenerated 3d orbitals are far from the nucleus of the ion and extremely sensitive to the environment of the transition element. As the orbitals orientation is different (figure 1.4), the interaction with the ligands through the potential \mathcal{V} will raise the degeneracy between the orbitals, depending on the ligands geometry.

For instance, in octahedral coordination, the $d_{x^2-y^2}$ and d_{z^2} orbitals (e_g in group theory) are oriented toward the ligands in the x, y and z directions whereas d_{xy} , d_{xz} and d_{yz} orbitals (t_{2g} in group theory) are pointing between the ligands (figure 1.4). Thus, the potential stabilizes the t_{2g} orbitals and destabilizes the e_g orbitals. The energy separation between both groups of orbitals is called crystal field splitting energy and is designated by Δ_o or 10 Dq (figure 1.5). The tetrahedral coordination has the inverse effect on the d orbitals. The crystal field splitting energy is $\Delta_t = \frac{4}{9} \Delta_o$ (figure 1.5). The distortion of the environment could lower again the local symmetry around the cation and raise degeneracy within t_{2g} or e_g orbitals (figure 1.5). This effect is known as the Jan-Teller effect, a distortion stabilizing the orbitals where electrons are located. As Fe environment in glasses is often considered to be five-fold coordinated (e.g. Rossano et al. (1999)), crystal field splitting in this environment is shown in figure 1.6.



Figure 1.4: Shape of the d atomic orbitals and orientation in a regular octahedron symmetry (octahedron corners represent the position of the ligands). Coloured parts represent the area where angular distribution probability of one electron is higher than 0.999.



Figure 1.5: Crystal field splitting of a transition element in tetrahedral, octahedral and distorted octahedral environments.



Figure 1.6: Crystal field splitting of a transition element in five-fold coordinated environments: trigonal bipyramidal and square pyramidal coordinations.

The crystal field splitting of the 3d orbitals makes electronic transitions between d orbitals possible by absorption of a photon at the energy of the splitting, in the UV-visible-near IR range.

The intensity of this absorption is given by the Beer-Lambert law:

$$O.D. = log(\frac{I_0}{I_T}) = \epsilon \cdot l \cdot c, \qquad (1.2)$$

where O.D. is the optical density or absorbance, I_0 is the intensity of incident light, I_T is the intensity of emergent light, l is the thickness of the sample (in cm), c the concentration in the absorbing species (in units such as mol \cdot L^{-1}) and ϵ the molar extinction coefficient (in units such as $L \cdot mol^{-1} \cdot cm^{-1}$) at the incident light wavelength. The extinction coefficient is related to the following integral:

$$I = \int \Psi_0 \cdot M \cdot \Psi, \tag{1.3}$$

where I is the intensity of the absorption, Ψ_0 is the ground state wave function, Ψ is the excited state considered for the transition and M is the electric dipole transition moment. The transition is allowed if the product is non equal to zero and forbidden otherwise. This equation is the mathematical translation of simple rules. The Laporte selection rule specify that the transition is forbidden if both states have the same symmetry (which means that both wave functions are symmetric or both are antisymmetric). The spin-multiplicity selection rule states that transition is forbidden if the number of spin changes. The geometry of the site also influence the intensity of a transition. A non-centrosymmetric site weaken the Laporte rule and the intensity of the transition is increased compared to centrosymmetric site. The expected intensity of a transition according to these rules is summarized in table 1.2 in the case of Fe crystal field transitions. Finally, to a lesser extent, temperature is also modifying the intensity. Indeed, the thermal vibrations are increased, and, as crystal field splitting is sensitive to the interatomic distances, the range of energy transitions is increased. The coupling between vibrational and electronic wave functions, called vibronic coupling, can also lead to a weakening of the Laporte selection rule, increased by increasing temperature.

Type of electronic transition	Corresponding situation with Fe	Relative molar extinction coefficient, ϵ
	Crystal Field Transitions	
Spin-forbidden, Laporte-forbidden, centrosymmetric site	Fe^{3+} , octahedral coordination	10^{-3} to 10^{0}
Spin-forbidden, Laporte-forbidden, acentric site	Fe^{3+} , tetrahedral coordination	10^{-1} to 10
Spin-allowed, Laporte-forbidden, centrosymmetric site	Fe^{2+} , octahedral coordination	10^0 to 10
Spin-allowed, Laporte-forbidden, acentric site	Fe^{2+} , tetrahedral coordination	$10-10^2$
	Electron Transfer Transitions	
Spin-allowed metal to metal	${\rm Fe}^{2+} \rightarrow {\rm Fe}^{3+}$ IVCT	10^2 to 10^3
intervalence charge transfer (IVCT) Spin-allowed, Laporte-allowed, oxygen to metal charge transfer(OMCT)	$O \rightarrow Fe^{3+}$	10^3 to 10^5

Table 1.2: Relative intensity of absorption bands for various cases of Fe electronic transitions, from Burns (1993).

Here, Fe^{2+} ([Ar] $3d^6$ electronic configuration) and Fe^{3+} ([Ar] $3d^5$ electronic configuration) are studied. The electrons can be distributed between 3d orbitals in various ways. Each non-equivalent way corresponds to a spectroscopic term, ^{2S+1}L . L is the total atomic orbital angular momenta (L = S, P, D, F, G, H or I) and S is the resultant spin quantum number. The spectroscopic terms for Fe^{2+} and Fe^{3+} are given in table 4.1 (appendices). Each free ion spectroscopic term is associated with crystal field states. The correspondence is given for Fe^{2+} and Fe^{3+} in octahedral and tetrahedral environment in table 4.2 (appendices). The energy of each crystal field state can be plotted versus the crystal field splitting energy, which depends of the inverse fifth-power of the metal-ligand distance. This representation, called the Tanabe-Sugano diagram (Tanabe and Sugano, 1954), gives the energy of a transition in a given environment and a given metal-ligand distance. If the environment is unknown, the transition energy can be used to deduce the environment and metal-ligand distances from the diagram. Examples of this diagram for Fe^{3+} matched with transitions in an optical absorption spectrum is given in figure 1.7.

Thus, thanks to the crystal field theory, optical absorption spectroscopy is a good tool to deduce the environment of Fe, from the absorption bands in optical absorption spectra of tektites and obsidians.



Figure 1.7: Energy level diagrams for Fe^{3+} matched to crystal field transitions of the polarized absorption spectrum of a yellow sapphire, from Burns (1993).

1.3.3 Charge Transfer and Vibrational Transitions

Optical absorption cannot always be only explained by crystal field theory. In transition element-bearing glasses, an intense transition in the near-UV region, called oxygen to metal charge transfer (OMCT) transition, can only be explained by correcting the main drawback of crystal field theory. The ligands are not anymore considered as point negative charge but orbital overlapping between transition metal orbitals and ligand orbitals is taken into account. This allows the prediction of OMCT transitions by photon absorption in the far UV area, because of the high energy difference between ligand orbitals (often p) and transition element orbitals (often d) involved in the transition. Nevertheless, the absorption edge may extend in the visible region. Indeed, they are fully Laporte-allowed and spin-allowed transitions and, thus, have high intensity (table 1.2). These transitions can thus influence the colour of the glasses studied.

Another kind of band, often centred in the visible area can appear in some Fe, Ti, Mn, or Cr-bearing materials. These bands results from an intervalence charge transfer (IVCT) transition. The photon absorption causes an electron transfer between two metals in different valence states, in adjacent coordination sites magnetically interacting. Two kinds of IVCT transitions can occur.

Homonuclear IVCT transitions involve single element in different oxidation state. For instance, between Fe^{2+} and Fe^{3+} in adjacent sites A and B:

$$Fe_A^{2+} + Fe_B^{3+} \to Fe_A^{3+} + Fe_B^{2+}.$$
 (1.4)

Other transitions are also possible such as $Ti^{3+} \rightarrow Ti^{4+}$ or $Mn^{3+} \rightarrow Mn^{2+}$. In the other hand, heteronuclear IVCT transitions involve two different cations. For examples, Fe^{2+} and Ti^{4+} :

$$Fe^{2+} + Ti^{4+} \to Fe^{3+} + Ti^{3+}.$$
 (1.5)

Among other examples, we can notice $Mn^{3+} \rightarrow Fe^{3+}$, $Mn^{2+} \rightarrow Fe^{3+}$ and $Fe^{2+} \rightarrow Mn^{3+}$ IVCT.

These transition have intensities similar to some allowed d-d transitions (table 1.2), moreover, the range of energy, in the visible area, overlap the energy of many d-d transition. Thus, it is sometimes difficult to make a difference between IVCT and d-d transitions. The combination of several features can however allow a distinction. The band energy must be in the range of energy known for the kind of IVCT expected. Moreover, an important width of the band is another argument. Another convincing proof is a spectacular decrease in intensity of the band with increasing temperature (Mattson and Rossman, 1987).

Finally, in the IR region, the low energy of the excitation created by the photon can lead to absorption by vibration or rotation of molecular groups as molecular water or hydroxyls (X-OH) in hydrated glasses. These absorptions lead to narrow bands with well-defined positions in the IR range.

1.4 Interest, Origin and Formation of the Selected Samples

Tektites samples among the types described above (section 1.1) have been chosen. First, a moldavite, from Bohemia (Czech Republic) formed 15 million years ago. It is a model tektites for many studies in Earth science and has also been widely studied owing to specific physical properties (Zavetova et al., 1989). The second tektite sample is a Muong Nong-type tektite from China, also called australasite tektite, formed 0.78 million years ago. The particular irregular shape and big size of these tektites compared to the others, as the layering and colour (Dressler and Reimold, 2001), makes it interesting to compare with regular tektites to check if any difference is seen in Fe speciation.

Six obsidian samples have been studied, due to the higher variety of occurrence of these glasses. Two Fe-rich samples, representing model obsidians from widely studied obsidian eruptions have been selected. An obsidian coming from Mono Craters (California, USA), an obsidian dome formed during an historical eruption dated at 1340 A.D. (Newman et al., 1988). The other sample comes from the Rocche Rosse lava flow in the island of Lipari (Italy), and has been dated between 524 A.D. and 562 A.D. (Gioncada et al., 2003). Two Fe-poor samples have also been chosen, one comes from Ecuador and the other from a lava dome in New Mexico (USA). They will be interesting to compare with the two previous classical Fe-rich samples because of the lightness of their colour. Finally, a round shaped obsidian sample , also called marekanite, have been studied. It comes from pyroclastic flows near from Cochiti, New Mexico (USA). The distinct conditions of formation compared to the four other samples explain this choice.



Figure 1.8: Photographs of the samples in thin section: (a) moldavite (tektite) from Bohemia (Czech Republic), (b) Muong Nong-type tektite from China, (c) dark obsidian from the Mono Craters (California, USA), (d) dark obsidian from the Rocche Rosse lava flow (Lipari, Italy), (e) light obsidian from New Mexico (USA), (f) light obsidian from Ecuador, (g) marekanite (obsidian) from Cochiti (New Mexico, USA).

2 Materials and Methods

2.1 Chemical Composition of the Samples

The selected tektite and obsidian samples had already been analysed by electron probe micro-analysis (EPMA) using a Cameca SX100 at Camparis Facility, Université Pierre et Marie Curie (tables 2.1 and 2.2). For each tektite and obsidian sample, Si, Al, Na, K, Mg, Ca, Ti, Mn, Fe and P have been analysed.

2.1.1 Tektites

The compositions of the moldavite from Czech Republic (Mol1) and of the Muong Nong-type tektite from China (TekCh1), also called australasite tektite, are given in table 2.1 (Rossano, pers. comm.).

	SiO_2	$\mathrm{Al}_2\mathrm{O}_3$	Na_2O	K_2O	MgO	CaO	TiO_2	MnO	FeO	P_2O_5	Total
Mol1	80.19	9.49	0.42	3.52	1.67	2.25	0.24	0.06	1.41	0.07	99.32
TekCh1	72.30	12.91	1.19	2.53	1.89	1.85	0.92	0.09	4.41	0.06	98.15

Table 2.1: Chemical composition of the textites studi	ied.
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2.1.2 Obsidians

The table 2.2 gives the composition of the obsidians from California (MonoE51), Lipari (Lip4), Ecuador (Ecu1), New Mexico (NM2) and Cochiti (MarCoch2) (Galoisy, pers. comm.).

	SiO ₂	$\mathrm{Al}_2\mathrm{O}_3$	Na_2O	K_2O	MgO	CaO	${\rm TiO}_2$	MnO	FeO	P_2O_5	Total
MonoE51	75.30	12.70	3.87	4.67	0.03	0.53	0.08	0.08	1.05	0.04	98.35
Lip4	70.14	12.65	4.05	5.13	0.05	0.75	0.06	0.05	1.66	0.05	94.59
NM2	76.17	12.59	4.02	4.53	0.04	0.44	0.02	0.08	0.58	0.03	98.50
Ecu1	76.94	13.03	3.80	4.50	0.07	0.56	0.02	0.06	0.53	0.03	99.54
MarCoch2	76.36	12.55	3.74	4.79	0.05	0.38	0.05	0.05	0.52	0.03	98.52

Table 2.2: Chemical composition of the obsidians studied.

2.2 Optical Absorption Spectroscopy (OAS)

2.2.1 Room Temperature Measurements

Fe speciation have been investigated in each glass using optical absorption spectroscopy in the UV-visible-near IR range using a PerkinElmer LAMBDA 1050 UV/Vis/NIR spectrophotometer.

The samples were cut and polished to get $5x5x0.5 \text{ mm}^3$ samples with parallel faces. Then, the spectra were measured in transmission from 300 to 2,500 nm (33,333 cm⁻¹ to 4,000 cm⁻¹) with a 2 nm step. The parameters were optimized to get spectra with the best signal-to-noise ratio within an acceptable recording time.

For each sample, one spectrum were measured without sample to get I_0 and another with a sample to get I_T . Then, we used the following relation:

$$O.D. = \log(\frac{I_0}{I_T}),\tag{2.1}$$

to obtain the optical density (O.D.). The wavelength scale was converted to a wavenumber scale. Finally, the thickness of each sample was carefully measured using a palmer micrometer and each spectrum was divided by the thickness of the sample (in cm) to get the absorption coefficient spectra.

2.2.2 High Temperature Measurements

High-temperature spectra were recorded using a Linkam heating stage placed into the spectrophotometer using a brand new microscope with Cassegrain optics, especially built for the experiment.

The figure 2.1 shows a schematic view of the assembly. The sample is introduced into the furnace. A hole in the centre of the furnace allows light transmission through the heating stage. The Cassegrain microscope deviates the beam emitted by the spectrophotometer in the direction of the sample. The light goes through the sample and is redirected by a second Cassegrain microscope in the direction of the detector. The focus is made at the bottom face of the sample, with a spot size of 150 μ m. Thus, the microscope allows the focalisation of the beam required to measure transmission spectra through the tiny furnace, at controlled temperature.



Figure 2.1: Photograph and schematic illustration of the experiment especially designed for high temperature measurements.

As the equipment has been received shortly before the beginning of this work placement, with researchers of the team, I did the tuning and made multiple measurements each sample to confirm the reproducibility of the method.

First, the microscope and the multiple reflections on the different mirrors create a significant background noise. This is particularly true in the area where the efficiency of the photomultiplicator of the spectrometer, which detects the transmitted photons, is low (figure 2.2, a, around $12,000 \text{ cm}^{-1}$). Thus, the gains and acquisition time had to be modified to get a better signal. Nevertheless, the noise is probably still too important after tuning to detect extremely weak absorption bands in this area. Then, an home made program, compiled with Igor Pro 6 TM, was used to correct the spectra. The spectrum was fitted around the noisy area using a tenth-degree polynomial function. After verification that the fit did not induce anomaly in the shape of the spectrum, the noisy region was replaced using the fitted spectrum. Moreover, using a binomial smoothing filter, the spectra were smoothed to remove the noise due to the high temperature experiment.

In some cases, the spectra show saturation due to the thickness of the sample (figure 2.2, a). In such cases, the thickness has been reduced to get an adapted absorption.

In addition, the inhomogeneity of certain samples and the presence of tiny air vesicles containing water vapor was also a problem (figure 2.2, a). Indeed, at high temperature, the disappearance of the vesicles, due to the probable diffusion of water in the matrix, provoked a diminution of the background absorption due to scattering on these

vesicles. Thus, each sample had to be carefully analysed to verify the homogeneity in the area of study.

Finally, for each temperature, at least two spectra had to be done (as explained section 2.2.1), I_T and I_0 . Indeed, the complex path of the beam, through the furnace, prevents the use of the I_0 given by the machine. But, at high temperature (500°C and 600°C) the emissivity of the furnace is non-negligible. Indeed, at these temperatures, the furnace emits light in the IR and red and creates artefacts on the spectra (figure 2.2, a). An additional transmission spectra, without light of the spectrophotometer was measured (I_F), at 500 and 600°C, in order to remove the emissivity of the furnace. The correction was made as follows:

$$O.D. = log(\frac{I_0 - I_F}{I_T - I_F}).$$
(2.2)



Figure 2.2: (a) Spectra of the obsidian sample Lip1, exhibiting the different drawbacks before tuning and corrections, (b) spectra of another piece of the same obsidian sample from Lipari, Lip4, after tuning and corrections.

For each sample, the spectra were recorded at fixed temperature between room temperature and 600°C with 100°C steps. Three additional spectra were measured at 500°C then 200°C and 25°C during cooling.

2.2.3 Absorption Bands Modelling

In order to separate the different transitions contributing to the absorption bands, the spectra were fitted using multiple Gaussian functions. Indeed, the assumption is generally made that absorption bands have Gaussian shapes in function of the energy (Burns, 1993). Each Gaussian at a specific position is then associated with a unique transition, and, as a result, to a unique oxidation state and environment.

The spectra were smoothed after measurement using Igor Pro 6 TM to remove noise. Then, the OMCT absorption edge in the visible and near UV area was fitted using a Gaussian shape. This Gaussian was subtracted from the spectrum. Then, a constant baseline was subtracted to take account of the different physical phenomena affecting light in this range of wavenumbers. Indeed, an important absorption background occurs in the samples studied due to coherent and incoherent light scattering, and reflections on the faces of the sample. Then, the fitting using multiple Gaussian was made using the multipeak fitting package of Igor Pro 6 TM.

Furthermore, some weak absorption bands due to the selection rules were hidden by the high intensity OMCT transitions. Thus, the edge of this band was fitted between $27,000 \text{ cm}^{-1}$ and $30,000 \text{ cm}^{-1}$ using an Urbach law:

$$\alpha(\nu) = \beta \cdot exp(\frac{h \cdot \nu}{E_U}) \tag{2.3}$$

with α the absorption coefficient (in cm⁻¹), ν the photon frequency (in s⁻¹), β a constant (in cm⁻¹), h the Planck constant (in m² · kg · s⁻¹) and E_U the Urbach energy (in J). This equation is empirical but satisfied in this range

for Fe-bearing glasses (Steele and Douglas, 1965). Then, this contribution was removed to detect the presence and position of weak absorption bands near the UV region.

2.2.4 Quantification of Glass Colour

Concerning colour, a qualitative estimation is often inadequate. Indeed, colour perception depends on the illuminant and the observer. Thus, photographs interpretation will differ for each observer and each lightening. In order to get quantitative information, an evaluation of colorimetry has been made using a standard procedure giving the $L^*a^*b^*$ coefficients in the colorimetric system defined in 1976 by the International Commission on Illumination (usually abbreviated CIE).

This method uses three colorimetric function \bar{x} , \bar{y} and \bar{z} (figure 2.3, a), analogous to the sensitivity function of the retinal cones in human eye. These three functions represent the observer. The integration of the product of the transmission spectra of the sample studied (T) with these functions in the visible region gives three new functions, X, Y and Z, the CIE tristimulus values:

$$X = \int_{380}^{780} T(\lambda) \cdot \bar{x}(\lambda) \cdot d\lambda \tag{2.4}$$

$$Y = \int_{380}^{780} T(\lambda) \cdot \bar{y}(\lambda) \cdot d\lambda \tag{2.5}$$

$$Z = \int_{380}^{780} T(\lambda) \cdot \bar{z}(\lambda) \cdot d\lambda.$$
(2.6)

Then, L*a*b* coefficient are get using the following expressions:

$$L^* = 116 \cdot f(\frac{Y}{Y_n}) - 16 \tag{2.7}$$

$$a^* = 500 \cdot \left(f(\frac{X}{X_n}) - f(\frac{Y}{Y_n}) \right)$$
(2.8)

$$b^* = 200 \cdot \left(f(\frac{Y}{Y_n}) - f(\frac{Z}{Z_n})\right)$$
(2.9)

Where
$$f(t) = \{ \begin{array}{ll} t^{\frac{1}{3}} & \text{if } t > \frac{6}{29}^{3}, \\ \frac{1}{3} \cdot (\frac{29}{6})^{2} \cdot t + \frac{4}{29} & \text{otherwise.} \end{array}$$
(2.10)

The X_n , Y_n and Z_n functions are the tabulated tristimulus values for the illuminant, here the spectrophotometer, chosen conventionally as t.

Thus, $L^*a^*b^*$ coefficients take into account both observer and illuminant and gives quantitative values of colorimetry for each absorption spectra of the samples studied. L^* represents the lightness of the color, it goes from 0 (black) to 100 (white). a^* is the green-red axis, going from negative values (green) to positive values (red). b^* is the blue-yellow axis, going from negative values (blue) to positive values (yellow). The quantification is good, but thickness dependent. Indeed, if absorbance is a linear function of sample thickness, according to Beer-Lambert law, $L^*a^*b^*$ coefficient are not. Thus, thickness of the samples has to be in the same range each time that two different samples are compared.

Sometimes results will be converted to be given in a chromaticity diagram in order to view the colour obtained (figure 2.3, b). Nevertheless, this diagram gives an idea of the colour but do not represent all colours perceptible. Thus, tables giving the L*a*b* values will also be given.



Figure 2.3: (a) CIE 1931 standard observer colorimetric functions, (b) A chromaticity diagram, x and y functions can be deduced from $L^*a^*b^*$ coefficients but the transformation is non bijective.

2.3 Electron Paramagnetic Resonance (EPR)

EPR is a spectroscopic method used to give insight into species bearing unpaired electrons. In the glasses studied, it concerns Fe^{3+} and in a lesser extent Mn^{2+} , in the absence of Ti^{3+} , only encountered in extraterrestrial glasses, formed under severe reducing conditions.

The unpaired electron studied has two spin states possible, up or down. In the presence of an external magnetic field H_0 , electron magnetic moment m_s can be aligned parallel $(m_s=-\frac{1}{2})$ or antiparallel $(m_s=\frac{1}{2})$ to the field. The energy of each state is given by:

$$E = m_s \cdot g \cdot \mu_B \cdot H_0, \tag{2.11}$$

with g a proportionality constant and μ_B the Bohr magneton. Thus, the presence of a magnetic field raises the degeneracy between both energy levels of the free unpaired electron. This phenomenon is called Zeeman effect. Then, alignment changes by absorption of a photon of the corresponding energy difference will be possible.

EPR spectroscopy uses this effect to measure light absorption. On the contrary of OAS, the frequency of the electromagnetic radiation is fixed and the magnetic field is scanned. Then, the first derivative of the absorption of the electromagnetic radiation by the sample is measured for each value of the magnetic field. The location of the absorption bands on the spectrum, given by the position where the sign of the first derivative changes, gives the g factor. This is essential to identify the species studied, nevertheless, it does not give information on the environment of the electron. Hopefully, interactions with surrounding magnetic particles, electrons and nuclei, called hyperfine interactions, modify the absorption spectrum and give information on the structures studied.

Here, the two tektites sample (a moldavite sample, Mol2, and a Muong Nong-type sample from China, TekCh2) were analysed. Compositions are expected to be the same than above because these samples are pieces of the samples analysed. X band frequency (9.75 GHz) spectra were recorded using a Bruker EMX plus EPR spectrometer. Magnetic field was scanned between 0 and 8000 Gauss.

3 Results

3.1 Optical Absorption Spectra at Room Temperature

3.1.1 Tektite Glasses

Optical absorption spectra of the moldavite sample (Mol1) and the Muong Nong-type tektite (TekCh1) at room temperature (figure 3.1, respectively a and b) present the following features:

- The background absorption coefficient is low for the moldavite spectrum (at least 2 cm⁻¹) and higher for the spectrum of the tektite from China (at least 10 cm⁻¹). It can be related to the darker colour in thin section of the TekCh1 sample compared to the Mol1 sample.
- In the two spectra, a high absorbance coefficient in the UV area is exhibited. It is due to the edge of a high intensity band centred in the far UV region. This is an OMCT transition (section 1.3.3) associated with O → Fe²⁺ or Fe³⁺ transitions, commonly observed in the spectra of Fe-bearing glasses and centred around 40,000 cm⁻¹ (Steele and Douglas, 1965). The edge is shifted toward the red region in the spectrum of the sample TekCh1. This can be the result of higher intensity of the OMCT absorption band, which spreads the band through the visible region of the spectrum, or to a lower energy of the absorption band.
- Two intense absorption bands, centred around 5,000 cm⁻¹ and 10,000 cm⁻¹, are observed in the IR region in both tektites spectra. Both are attributed to Fe²⁺ according to comparisons with reference minerals (Burns, 1993) and other synthetic Fe-bearing glasses (Fox et al., 1982).



Figure 3.1: Optical absorption spectra measured at room temperature (arrows are indicating the species at the origin of each band): (a) Mol1, (b) TekCh1. At the top of the graph, the positions of the IR (less than 12,500 cm⁻¹), visible (between 12,500 cm⁻¹ and 25,000 cm⁻¹) and UV (more than 25,000 cm⁻¹) regions is indicated.

 Fe^{2+} IR absorption bands have been fitted using Gaussians, in order to separate the different transitions contributing to absorption. Both curve fittings are similar, but there is not a unique solution. One solution may consist of three Gaussian components centred around 5,300 cm⁻¹, 8,400 cm⁻¹ and 10,500 cm⁻¹ (Gaussian T1, T2 and T3 respectively) (figure 3.2).

No other absorption bands seem to appear in the spectra. Nevertheless, in order to check this assertion, the OMCT absorption edge has been fitted by Urbach law and the residual error is shown in figure 3.3. Thus, the presence of two weak absorption bands at 22,400 cm⁻¹ and 18,000 cm⁻¹ in the spectrum of the Muong Nong-type tektite is revealed. Even weaker absorption bands are revealed at 18,000 cm⁻¹ and 20,000 cm⁻¹ in the spectrum of the moldavite sample. These positions correspond to Fe^{3+} bands, by comparison to spectra of reference minerals (Hofmeister and Rossman, 1984) and spectra of Fe-bearing synthetic glasses (Hannoyer et al., 1992).



Figure 3.2: Modelling of the absorption band due to Fe²⁺ by multiple Gaussian fitting: (a) Mol1, (b) TekCh1.



Figure 3.3: Fitting of the OMCT absorption edge by Urbach law, at room temperature: (a) Mol1, (b) TekCh1. Residual error is indicated at the top of each graph.

3.1.2 Obsidian Glasses

Optical absorption spectra of the six obsidian glasses studied, MonoE51, Lip4, NM2, Ecu1 and MarCoch2 (figure 3.4, respectively a, b, c and d and figure 3.5, e) present analogies with tektite spectra at room temperature, but new and different bands also appear:

- The two spectra of Fe-rich obsidians (MonoE51 and Lip4) have a high background absorption (at least 5 cm⁻¹). The background absorption is lower for the spectra of the other samples, around 1 cm⁻¹ for the minimal value. This is in agreement with visual appearance of Fe-rich obsidians, darker compared to Fe-poor obsidian (figure 1.8, section 1.4).
- The near-UV edge, already observed in tektites, is exhibited in all of the obsidian spectra. It can be attributed to OMCT transitions due to Fe.
- As opposed to tektites, five weak absorption bands are visible in obsidian spectra in the visible range, without fit of the edge by Urbach law. The energy of these absorption bands is quite similar between the samples and located around 18,000 cm⁻¹, 20,500 cm⁻¹, 22,500 cm⁻¹, 24,000 cm⁻¹ and 27,000 cm⁻¹. They are attributed

to Fe^{3+} , by comparison with an albite (NaAlSi₃O₈) glass bearing Fe (figure 3.5, f), where they are attributed to Fe^{3+} (Hannoyer et al., 1992).

- A broad absorption band, not much intense, centred around 17,500 cm⁻¹ is exhibited. This band is quite unexpected considering the wide range of spectra of Fe-bearing silicate glasses studied presenting a transmission window in this region. Nevertheless, the position of the band is in good agreement with the existence of an IVCT transition observed in this range of energy in many mineral compounds (Mattson and Rossman, 1987).
- An intense band is situated in the IR range of every spectra. The position and intensity of the band, by comparison to reference minerals and glasses make it attributable to Fe²⁺, such as above. But, unexpectedly in a glass, the band shape is symmetric and nearly Gaussian.
- The obsidian samples spectra exhibit also three narrow bands at 4,500 cm⁻¹, 5,200 cm⁻¹ and 7,100 cm⁻¹ that originate from combination bands of X-OH groups around 4,500 cm⁻¹, stretching and bending of molecular water at 5,200 cm⁻¹ and OH stretching modes at 7,100 cm⁻¹ (Newman et al., 1986).



Figure 3.4: Optical absorption spectra measured at room temperature, arrows are indicating the species at the origin of each band: (a) MonoE51, (b) Lip4, (c) NM2, (d) Ecu1. At the top of the graph, the positions of the IR (less than 12,500 cm⁻¹), visible (between 12,500 cm⁻¹ and 25,000 cm⁻¹) and UV (more than 25,000 cm⁻¹) regions is indicated.



Figure 3.5: Optical absorption spectra measured at room temperature, arrows are indicating the species at the origin of each band: (a) MarCoch2, (b) an albite (NaAlSi₃O₈) glass bearing Fe. The graph (b) is represented between 16,000 cm⁻¹ and 28,000 cm⁻¹ to show the location of the absorption bands associated with Fe³⁺ observed in this region.

In order to identify the different transitions contributing to the IR absorption band, multiple Gaussian fitting has been made (figure 3.6). Only two modelling are shown because they are all similar. When narrow Gaussian contributions due to water vibrational transitions (W1, W2 and W3) are removed, one intense Gaussian (O1), centred around 9,000 cm⁻¹ is needed to fit the data. One would notice that the fitting is far from perfect, but the addition of other Gaussian functions does not improve significantly the fit if realistic positions and widths are kept.



Figure 3.6: Fe^{2+} absorption band modelling at room temperature by multiple Gaussian fitting: (a) MonoE51, (b) NM2.

3.2.1 Tektite Glasses

In tektite glasses, the evolution of the optical absorption spectra measured between room temperature and 600°C (figure 3.7, a and b) reveals three important changes:

- A red-shift of the OMCT edge is observed. It could results from broadening of the OMCT transition absorption band when temperature increases, as expected from theory (section 1.3.2).
- IR absorption band broadens and intensity is lowering, in good agreement with the influence of temperature on absorption bands due to d-d electronic transitions (section 1.3.2).
- Two isobestic points are observed at 4,600 cm⁻¹ and 6,200 cm⁻¹. The presence of isobestic points is usually associated with reactions between different species. Here, it could be between Fe²⁺ environments associated with the Gaussians T1, T2 and/or T3.



Figure 3.7: Optical absorption spectra measured between room temperature and 600°C with a 100°C step, (arrows are indicating the species at the origin of each band): (a) Mol1, (b) TekCh1. Three additional spectra, captioned "return", have been measured during cooling, at fixed temperatures, 500°C, 200°C and room temperature.

To verify the evolution of the Fe^{2+} environment, the evolution of the location, width and intensity of the Gaussian functions T1, T2 and T3 has been followed by curve fitting at each temperature. The location of each absorption bands is steady whereas width is increasing with increasing temperature, as expected (section 1.3.2). In the sample TekCh1, T1 and T3 intensities decrease with increasing temperature whereas T2 intensity increases (figure 3.8). This trend is not well reproduced in the Mol1 sample.



Figure 3.8: Evolution of the intensity of the Gaussians contributing to the Fe^{2+} IR absorption band with the temperature: (a) TekCh1, Gaussian function T1, (b) TekCh1, Gaussian function T2, (c) TekCh1, Gaussian function T3.

3.2.2 Obsidian Glasses

The main features appearing when optical absorption spectra are measured at increasing temperatures between 25°C and 600°C in the six obsidian samples (figure 3.9) are summarized as follows:

- A red-shift of the UV-edge is observed, such as in previous samples. It could also be associated with a broadening of the OMCT absorption band. This shift is progressively hiding the Fe³⁺ bands, but they probably do not disappear. This is confirmed by the presence of the Fe³⁺ absorption bands when spectra are measured after heating.
- Two isobestic points are visible, at the intersection of the different spectra around 12,000 cm⁻¹ and 22,000 cm⁻¹. It reveals the existence of a reaction leading to the dramatic disappearance of the large absorption band centred around 17,500 cm⁻¹.
- Two different behaviours are observed for the Fe²⁺ absorption band. In Fe-rich samples (MonoE51 and Lip4), as expected when thermal agitation increases, IR absorption bands intensity and width increase. In Fe-poor samples NM2 and MarCoch2, with the exception of Ecu1, the intensity is unexpectedly increasing with increasing temperature.
- The intensity of the OH vibrational modes slightly decreases with temperature and the vibrational band of molecular water disappears in Fe-rich samples, probably because of an equilibrium between hydroxyl and molecular water concentrations.



Figure 3.9: Optical absorption spectra measured between room temperature and 600°C with a 100°C step: (a) MonoE51, (b) Lip4, (c) NM2, (d) Ecu1, (f) MarCoch2. Three additional spectra, captioned "return", have been measured during cooling, at fixed temperatures, 500°C, 200°C and room temperature.

3.3 Glass Colour Results

3.3.1 Colour at Room Temperature

The colour derived from absorption spectra at room temperature (figure 3.10, table 4.3 and table 4.4, appendices) do not reflect completely what can be observed to the naked eye (figure 1.8). TekCh1, brownish on the photograph is situated in the orange part of the diagram, as expected. Moreover, Mol1 is greener than the obsidian samples. But, the other samples are light violet. As the quantification is thickness dependent and spectra are measured in thin section, all the samples are in the centre of the diagram, reflecting the lightness of the colour and probably explaining the little range of colours obtained.



Figure 3.10: Position of each sample in the chromaticity diagram (right graph: enlargement of the left diagram).

3.3.2 High-temperature Influence on Colour

Quantification of colour at high temperature, impossible to make by photography *in situ*, has also been made using colorimetry on high temperature optical absorption spectra (table 4.3 and table 4.4, appendices). The L* component, characterising the lightness of the sample, exhibits opposite trends with temperature between the group of obsidian samples in the one hand and the group of tektite glasses in the other hand (figure 3.11, a and b, which represents an example of this evolution in Mol1 and MonoE51, respectively). A darkening of the Mol1 tektite is observed with increasing temperature, as in the other tektites and in synthetic samples (table 4.3). On the contrary, MonoE51 is lightening with increasing temperature as the other obsidian samples (table 4.4).



Figure 3.11: Evolution of the L^{*} CIE parameter with temperature: a) Mol1, b) MonoE51. The colour scale is a guide indicating that increasing L^{*} parameter is associated with increasing lightness of the colour.

3.4 Electron Paramagnetic Resonance

In order to obtain further information on Fe^{3+} environment and determine whether or not Fe^{3+} can be at the origin of the slight absorption bands observed in the UV-region of the optical absorption spectra of tektites, EPR spectra have been measured on tektites (figure 3.12, a, Mol1 and b, MonoE51).

An intense band is observed at H=1500 G (g=4.3 obtained from the formula of the section 2.3). This band has been attributed to Fe^{3+} (Castner et al., 1960), confirming the presence of ferric iron in these samples. Moreover, another weak band at H=3400 G (g \simeq 2) is present and is attributed to Mn^{2+} (Van Wieringen, 1955). Usually, a weak band with a different shape at H=3300 G (g \simeq 2) is observed when Fe^{3+} is present (Castner et al., 1960). It is probably hidden in tektites by the Mn band.



Figure 3.12: Electron paramagnetic resonance spectra at room temperature measured between 0 and 8,000 G: a) Mol1, b) TekCh1.

4 Discussion

4.1 Tektite Glasses

4.1.1 Iron Speciation in Tektites

Tektite spectra do not exhibit apparent Fe^{3+} bands (figure 3.1). Thus, Fe^{3+} content is probably low in these samples. Moreover, d-d electronic transitions are Laporte-forbidden and, as Fe^{3+} electronic configuration is [Ar] d⁵, the transitions are also spin-forbidden (section 1.3.2). Nevertheless, the removal of the OMCT-edge on Muong Nong-type tektite spectrum reveals the presence of two extremely weak bands (figure 3.3). In the case of the moldavite sample, even weaker bands are detected. All these bands are in good agreement with Fe^{3+} absorption bands positions (Hannoyer et al., 1992). The presence of the Fe^{3+} absorption band at g=4.3 in EPR spectra of the two tektites (figure 3.12, a and b) can also be detected. Thus, in spite of the weakness of Fe^{3+} absorption bands, it confirms that they are not artefacts due to measurement.

In terms of environment, the 22,400 cm⁻¹ absorption band, visible in the TekCh1 absorption spectrum, is generally attributed to Fe³⁺ in tetrahedral coordination in spectra of synthetic glasses (Steele and Douglas, 1965; Hannoyer et al., 1992). The 20,000 cm⁻¹ absorption band observed in the spectrum of the moldavite could correspond to a band observed at 20,500 cm⁻¹ in some synthetic glasses (Kurkjian and Sigety, 1968). This band is also associated with a tetrahedral coordination of Fe³⁺. Finally, the 18,000 cm⁻¹ absorption band is not observed in usual spectra of synthetic glasses (Hannoyer et al., 1992). However, this position corresponds to an absorption band attributed to Fe³⁺ in octahedral coordination generally situated at lower energies in synthetic glasses spectra (Hannoyer et al., 1992).

The presence of ferrous iron leads to intense absorption bands visible in the IR region in the two spectra of tektites (figure 3.1). As Fe^{2+} is a d⁶ ion, this transition is only Laporte-forbidden but spin-allowed (section 1.3.2), explaining the intensity of the band compared to Fe^{3+} . Nevertheless, the broad bands associated with each Fe^{2+} environment are superposed. Thus, the study is complex and no general agreement exists concerning the different contributions involved in the absorption bands observed in Fe-bearing glasses.

Using a comparison with the M2 site of orthopyroxens (Bancroft and Burns, 1967), an explanation has been given to the presence of the absorption band centred around 10,000 cm⁻¹ and to the shoulder centred around 5,000 cm⁻¹ (Fox et al., 1982). The high distortion of the octahedral site M2 leads to an important splitting of the ${}^{5}E_{g}$ levels of Fe²⁺ (section 1.3.2). Thus, the optical absorption spectrum exhibits two separated absorption bands at 5,380 cm⁻¹ and 10,970 cm⁻¹, in good agreement with the position of the absorption band in tektite spectra. But, three Gaussian can be used to fit the Fe²⁺ absorption band, T1, T2 and T3 (figure 3.2), which could be associated with three different transitions. Moreover, the behaviour of the Gaussian function T1, which intensity decreases with increasing temperature, whereas T2 intensity is steady (figure 3.8) can only be explained by the presence of two different sites. Both observations exclude this first explanation.

Another explanation using comparison with reference mineral spectra is in better agreement. The band T1, centred around 5,000 cm⁻¹, is in relative agreement with the positions of tetrahedral Fe²⁺ absorption band in reference minerals as in spinel (Fe:MgAl₂O₃) at 4,830 cm⁻¹ or staurolite (Fe₂²⁺Al₉O₆(SiO₄)₄(O,OH)₂) at 5,100 cm⁻¹ (Burns, 1993). This band could thus be associated with tetrahedral Fe²⁺. The two other Gaussian functions, T2 and T3, centred around 8,500 cm⁻¹ and 11,000 cm⁻¹ can be associated with a ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$ transition in octahedral site distorted by Jan-Teller effect as in periclase with two absorption bands at 10,000 cm⁻¹ and 11,600 cm⁻¹ (Burns, 1993). Nevertheless, considering that the intensity of the Gaussian function T3 decreases with increasing temperature while T2 intensity is steady in the absorption band of the TekCh1 spectrum, two different environments probably exist.

Some complementary information are known on Fe^{2+} environment in tektites. X-ray absorption spectroscopy at the Fe pre-edge and extended X-ray absorption fine structure on tektites (Giuli et al., 2002) have revealed an average coordination of 4.5, in good agreement with Mössbauer spectroscopy (Rossano et al., 1999). Thus, part of Fe^{2+} is in tetrahedral environment, which is still in agreement with the association of the T1 Gaussian function to tetrahedral Fe^{2+} . But, the average coordination of Fe^{2+} imply to consider 5-fold coordination. Indeed, if 75% of Fe^{2+} is in tetrahedral environment and 25% of Fe^{2+} in octahedral environment, this should lead to an intensity of the tetrahedral absorption band centred at 5,000 cm⁻¹ band higher than the 10,000 cm⁻¹ absorption band. Indeed, tetrahedral site is acentric and weaken Laporte selection rule whereas octahedron is centrosymmetric. Thus, T2 and T3 probably results from 5-fold coordinated environments which is in agreement with crystal field energy splitting in penta-coordinated environments (Pavel et al., 1994). The existence of one 5-fold and one 6-fold coordinated sites is also possible.

In summary:

- Ferric iron concentration in the tektites studied is poor, but Fe^{3+} is present as shown by EPR.
- Fe^{3+} is present in tetrahedral coordination, with a possible contribution of six-fold coordinated Fe^{3+} .
- Ferrous iron is in tetrahedral and 5-fold coordinated environments, possibly associated with a minor content of 6-fold coordinated Fe^{2+} .

4.1.2 Tektite Colour and Iron Environment

The moldavite sample spectrum exhibits a transmission window in the visible region (figure 3.1, a). Indeed, no absorption band occur between the Fe^{2+} intense absorption band in the near IR-region and the UV-edge of the absorption band associated with OMCT transition. The absorption in the far-red and far-blue region associated with these two features, combined with high sensitivity of human eye to green colour explains the green coloration of this tektite. Moreover, the lightness and transparency is explained by the low background absorption.

In comparison, Muong Nong-type tektite transmission window is reduced, due to the red-shift of the OMCT absorption edge. The higher Fe concentration of this tektite, probably leading to this shift, results in the brownish colour of this tektite. Moreover, the high background absorption makes this tektite darker.

Thus, colour differences between both tektites are not associated with different Fe environment but only with Fe concentration.

Increasing temperature shifts the OMCT absorption bands toward red region in both tektites spectra. The absorption of visible light is increased, leading to a darkening of the tektites colour. Moreover, the transmission window is reduced and blue wavelength absorption is increased, which redden the colour of tektites and explains the increase of the a* parameter with temperature (table 4.3, appendices).

4.1.3 Significance of Iron Oxidation and Environment in the Formation of Tektites

In tektites, the most striking property is the low ferric iron content. Indeed, Fe^{3+} is barely observable in optical absorption spectroscopy. EPR measurements have been used to confirm the presence of ferric iron. The observation of Fe^{3+} in EPR spectra of the two tektites is quite surprising considering Mössbauer spectroscopy which did not detect the presence of Fe^{3+} (Rossano et al., 1999). Nevertheless, the sensitivity of EPR is higher as it is only sensible to Fe^{3+} whereas in Mössbauer spectra, the Fe^{3+} contributions can be hidden by Fe^{2+} peaks. Moreover, even if the ferric iron content is below the uncertainty limits of the method, wet chemical analysis gives untill 5 % of ferric iron in moldavite and 9 % in Muong Nong-type tektites (Rossano et al., 1999). Finally, X-ray absorption spectroscopy measurements also revealed Fe^{3+} presence between 0 and 10 % (Giuli et al., 2002). Thus, tektites were formed in highly reducing conditions, far from the conditions known in the usual terrestrial atmosphere.

Moreover, the presence of 5-fold coordination of Fe^{2+} shown above, and the differences with synthetic glasses, where 6-fold coordinated Fe is often described (Fox et al., 1982; Ades et al., 1990)) are probably the consequence of the hyperquenching of Fe^{2+} . Indeed, during tektites formation, the quenched liquid stays near to the average 5-fold coordination which would be observed at a given time in a liquid Stebbins (1991).

Finally, the dehydration, shown by the absence of water vibrational bands compared to obsidians (figure 3.4) is probably the result of a vaporisation of water during the impact which is then excluded from the melt.

All these observations reflect an extremely fast quenching of the melt in reducing conditions resulting from a blow up of the atmosphere just after the impact leading to the formation of tektites.

4.2 Obsidian Glasses

4.2.1 Iron Environment in Obsidians

In obsidian spectra, ferric iron presence is shown by the presence of five absorption bands. The position of these bands is highly similar to the Fe³⁺ absorption bands attributed in reference minerals and glasses. For instance, in albite (NaAlSi₃O₈) glasses bearing Fe, the presence of Fe³⁺ is evidenced by five narrow and weak bands at 18,000 cm⁻¹, 20,500 cm⁻¹, 22,800 cm⁻¹, 24,000 cm⁻¹ and 26,400 cm⁻¹ (figure 3.4, f). By analogy with different studies on reference minerals (Burns, 1993), and particularly on feldspars (Hofmeister and Rossman, 1984), the three bands at 22,800 cm⁻¹, 24,000 cm⁻¹ and 26,400 cm⁻¹ are attributed to the following transitions in tetrahedral coordination:

$$22,800 \ cm^{-1}: \ {}^{6}A_{1}(S) \ \to \ {}^{4}E(D) \tag{4.1}$$

$$24,000 \ cm^{-1}: \ {}^{6}A_{1}(S) \ \to \ {}^{4}T_{2}(D) \tag{4.2}$$

$$26,400 \ cm^{-1}: \ {}^{6}A_{1}(S) \ \to \ {}^{4}A_{1} \ {}^{4}E(G).$$

$$(4.3)$$

The 20,500 cm⁻¹ can be explained by a ${}^{6}A_{1}(S) \rightarrow {}^{4}T^{2}(G)$ transition in tetrahedral environment (Hannoyer et al., 1992). Nevertheless, by analogy with feldspar, the bands at 20,500 cm⁻¹ and 18,000 cm⁻¹ can be attributed to octahedral environment (Hofmeister and Rossman, 1984). The higher intensity of the three absorption bands at 22,800 cm⁻¹, 24,000 cm⁻¹ and 26,400 cm⁻¹ compared to the absorption bands at 18,000 cm⁻¹ and 20,500 cm⁻¹ confirms this assessment because Fe³⁺ is in an acentric site, weakening the Laporte selection rule.

Ferrous iron in obsidian spectra only exhibits a symmetric and near Gaussian absorption band (figure 3.4). It can be fitted by one Gaussian function O1, centred around 9,000 cm⁻¹ (figure 3.6). It can only be explained by a specific and uncommon environment of Fe^{2+} in these glasses compared to tektites and synthetic glasses. This shows unambiguously that Fe^{2+} is in non-distorted octahedral environment, considering crystal field theory. Indeed, this theory predicts only one transition around 10,000 cm⁻¹ for Fe^{2+} in octahedral environment. Nevertheless, in minerals, the symmetry of the site is lowered by Jan-Teller effect and the band is always splitted. Thus, Fe^{2+} incorporation is specific to these obsidians. This is maybe the result of the beginning of a nucleation process creating a well-organised environment for Fe. This is in agreement with Mössbauer spectroscopy which exhibits contributions of Fe^{2+} in octahedral sites only (Spiering and Seifert, 1985).

To sum up, obsidian absorption spectroscopy of obsidian reveals:

- the presence of octahedral and tetrahedral environment of Fe^{3+} .
- the incorporation of Fe^{2+} in a highly symmetric octahedral site.

4.2.2 Evidence of Iron Nano-clusters in Obsidians and Implication on Colour

Obsidian deep black colour in bulk can be explained using two phenomena observed in optical absorption spectra. First, the important background absorption of the obsidian spectra is involved (figure 3.4). Indeed, the minimal absorption coefficient of MonoE51, around 5 cm⁻¹, is more than twice the one of a tektite with a similar Fe content, as the moldavite (around 2 cm⁻¹). This could be associated with the presence of micronic magnetite crystals (Fe₂³⁺Fe²⁺O₃) visible in microscopy (Ericson et al., 1975). Indeed, micronic crystals have been used to explain the colour of rare "fire" obsidians (Ma et al., 2007). However, in regular obsidian, even if Fe is considered only as magnetite, a simple calculation shows that crystals would represent only 1% in volume of the obsidian. Indeed, considering the following hypothesis:

- Fe is only incorporated in magnetite, which is a strong assumption, needing the good Fe^{2+}/Fe^{3+} ratio and no Fe incorporation in the glass network
- Fe wt% in obsidians is 2 wt%, which is among the highest percentage in the samples studied

•
$$\rho_{obs} = 2500 \text{ kg} \cdot \text{m}^3$$

• $\rho_{magn} = 5200 \text{ kg} \cdot \text{m}^3$.

Then, the calculation gives:

$$m_{magn} = 0.02 \cdot m_{obs} \iff \rho_{magn} \cdot V_{magn} = 0.02\rho_{obs} * V_{obs} \iff V_{magn} = 0.01 \cdot V_{obs}. \tag{4.4}$$

Thus, considering that magnetite is a cubic crystal, having consequently an isometric morphology, absorbing all incident light with a 10 micron size in the obsidian matrix (Ericson et al., 1975), the maximum absorption is 10% which is insufficient to explain the opacity (figure 4.1).



Figure 4.1: Illustration of the absorption of light by an imaginary obsidian containing an overestimated proportion of magnetite crystals.

The second important feature influencing colour is the wide band centred around $17,500 \text{ cm}^{-1}$ (figure 3.4). This band is absent from tektite absorption spectra (figure 3.1) which exhibit a transmission window centred on the green part of the electromagnetic spectrum. The band is expected to be the result of an IVCT (section 1.3.3). The presence of Fe and Ti in the chemical composition of the glass gives two possible reactions:

$$Fe_A^{2+} + Fe_B^{3+} \to Fe_A^{3+} + Fe_B^{2+}$$
 (4.5)

$$Fe^{2+} + Ti^{4+} \to Fe^{3+} + Ti^{3+}.$$
 (4.6)

Ti proportion is relatively low but the element is generally closely associated with Fe and is probably playing a part in the IVCT. However, even if Mn is present, the only IVCT implying Mn possible is $Mn^{2+} \rightarrow Fe^{3+}$ but this has not been observed in natural minerals (Burns, 1993). Thus, it is quite improbable in the obsidian studied.

IVCT is quite uncommon in Fe bearing glasses but several arguments are in favour of this origin. The band energy which is in the interval of observed $Fe^{2+} \rightarrow Fe^{3+}$ IVCT in reference compounds, between 9,700 and 18,500 cm⁻¹, is in good agreement (Burns, 1993). The energy of this transition is quite high in the interval which is in favour of an $Fe^{2+} \rightarrow Ti^{4+}$ IVCT in obsidians. Indeed, the energy of these transitions in minerals is between 17,000 and 24,000 cm⁻¹, which could shift the position of the absorption band toward higher energies in the samples studied. In addition, the width of the band, around 6,000 cm⁻¹ is a proof of the impossibility of a metal transition band (Mattson and Rossman, 1987) and, thus, another argument in favour of an oxygen to metal charge transfer transition. The best evidence of this transition is the spectacular decrease in intensity of the band with increasing temperature between 0 and 1,000 K (Faye et al., 1968). The decrease of the intensity of the IVCT absorption band between 0 K and room temperature in obsidians has already been shown (Galoisy et al., 2013, in prep.). The original experiment used here to measure high temperature spectra shows that this decrease continues between room temperature and 600°C (figure 3.4). All these arguments using optical absorption spectroscopy prove the existence of this IVCT transition.

This observation, associated with the unusual environment of Fe^{2+} in the glass network let think that Fe cations are not homogeneously spread in the network structure but are brought together in clusters. The presence of superparamagnetic domains, already long been shown in obsidians by EPR spectroscopy (Calas and Petiau, 1983), is in good agreement with the existence of these clusters.

The disappearance of the IVCT signal with the temperature could be associated with a dissolution of Fe clusters when temperature increases. Nevertheless, the disappearance is already pronounced at 200°C, far below the glass transition temperature. In addition, the reversibility of the process is excluding this explanation. Thus, this is an electronic phenomenon. The probable increase of thermal vibration is possibly the cause, with a rupture of the magnetic coupling between adjacent cations leading to the disappearance of the band.

This second feature is important in the deep black colour obsidian. Indeed, when temperature increases, the disappearance of this band is associated with a diminution of the L* parameter (figure 3.11). The correlation between both phenomena is probable because this band covers most of the visible area, thus a disappearance would lighten the colour of the sample, which is translated by a decrease of the L* parameter. This is confirmed by the increase of this parameter with increasing temperatures in tektites (table 4.3). Thus, whereas OMCT red-shift is also observable in obsidians, the colour of these samples is still lightening with increasing temperature. This confirms the importance of the IVCT band in the darkening of the obsidians.

Moreover, these clusters could take part in the background absorption. Indeed, using the same calculation as above on magnetite absorption but with anisotropic nanophases or clusters, it could lead to a high level of absorption.

In summary, the highlight of an IVCT in obsidians using high temperature optical absorption measurements revealed the presence of Fe nanoclusters, confirmed by unusual Fe^{2+} speciation in obsidians discussed above and by EPR measurements (Calas and Petiau, 1983). The colorimetry confirmed that these clusters are probably at the origin of the deep black colour of obsidians.

4.2.3 Implications of Unusual Iron Speciation in Obsidians Formation

In obsidians, at least a part of Fe cations are associated in clusters in the glass network. These clusters could have an organised structure, considering the highly symmetrical environment of Fe^{2+} . Moreover, the presence of 6-fold coordinated Fe^{2+} , of tetrahedral and octahedral Fe^{3+} and of an IVCT are indication of edge-sharing between both species. Indeed, the interatomic distance required to an IVCT transition imply that cations are close neighbours. In addition with the observation of rare crystals of magnetite in the vitreous matrix, this is leading to the hypothesis of the presence of nuclei of protomagnetite or other Fe-bearing nanophases which remained as nuclei. Indeed, magnetite ($Fe^{2+}Fe_2^{3+}O_3$) contains both ferric and ferrous iron and in this structure called inverse spinel, edge-sharing Fe^{2+} and Fe^{3+} environments are present. Moreover, magnetite also exhibits IVCT (Fontijn et al., 1997).

Thus, volcanic glasses are able to keep a memory of their conditions of formation. Moreover, slow cooling rates of natural volcanic events associated with the important viscosity of highly silicic melts as the one forming obsidians could give a frozen picture of the nucleation process.

Conclusion

The analysis of the glasses by optical absorption spectroscopy revealed information on the origin of colour associated with specific Fe speciation. The comparison between the spectra of tektites and obsidians associated with the temperature measurements indicate that the black colour and intense light absorption of obsidians is due to the presence of clusters of Fe oxides. They could be nuclei of magnetite quenched at the glass transition before crystallization starts. This shows an interesting pattern of volcanic glasses which are able to keep a memory of their conditions of formation. Thus, obsidians are original glasses compared to synthetic glasses but also to tektites, the fast cooling of which makes them resembling to synthetic ones.

In tektites, Fe^{2+} speciation is completely different from the speciation in obsidians. Tetrahedral and five-fold coordinated Fe^{2+} are present in contrast with the regular octahedral site in obsidians. This is the environment generally observed in synthetic glasses, indicating the fast quenching preventing the beginning of a nucleation, as in obsidians. Moreover, Fe oxidation state reveals a low Fe^{3+} content indicating that, during the meteoritic impact forming tektites, the atmosphere is blown. Indeed, the low oxygen content due to the possible absence of atmosphere leads to reducing conditions in the melt.

In order to go further in this study, different interesting studies could be lead:

- Accurate calculations of Fe^{2+}/Fe^{3+} ratio in tektites using EPR spectroscopy and models of oxidation reactions of Fe in melts could be used to determine the oxidation state of the atmosphere during tektite formation.
- As the interpretation of optical absorption spectra is complex, it could be interesting to complete this study with other methods as X-ray absorption spectroscopy at Fe-edges on obsidians to get more information on Fe environment. Nevertheless, as in these glasses Fe can be 4, 5 or 6-fold coordinated and ferric or ferrous most of the techniques are not able to distinguish between these species. Thus, only X-ray absorption near-edge spectroscopy (XANES) can be used so far.
- Modelling of d-d electronic transitions is another trail to explore. It would be interesting, but it is difficult considering the low energy difference between splitted d orbitals.
- High-pressure measurements of optical absorption spectra using a diamond anvil cell adapted using the same microscope could also reveal information on Fe environment and interatomic distances. Indeed, crystal field transitions, but also IVCT and OMCT transitions, are dependent of interatomic distances, and, consequently, of pressure.
- To understand in greater depth the origin of the black color of obsidians, as the presence of clusters corresponding to nuclei is suspected, a study using transmission electronic microscopy (TEM) on obsidian glasses would be informative. It could make it possible to find amorphous Fe oxide of nanometric size, proof of the existence of nuclei and could give more information on their actual nature.

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Appendices

Configuration	Ground term	Excited terms
$Fe^{2+} (d^6)$	${}^{5}\mathrm{D}$	${}^{3}H, {}^{3}G, {}^{3}F, {}^{3}F, {}^{3}D, {}^{3}P, {}^{3}P, {}^{1}I, {}^{1}G, {}^{1}G, {}^{1}F, {}^{1}D, {}^{1}D, {}^{1}S, {}^{1}S$
$Fe^{3+} (d^5)$	${}^{6}\mathrm{S}$	${}^{4}G, {}^{4}F, {}^{4}D, {}^{4}P, {}^{2}I, {}^{2}H, {}^{2}G, {}^{2}G, {}^{2}F, {}^{2}F, {}^{2}D, {}^{2}D, {}^{2}D, {}^{2}P, {}^{2}S$

Table 4.1: Spectroscopic terms of Fe^{2+} and Fe^{3+} .

Free-ion spectroscopic terms	Crystal field states in tetrahedral coordination	Crystal field terms in octahedral coordination
S	A_1	A_{1q}
Р	T_{1}	T_{1q}
D	$T_2 + E$	$T_{2g} + E_g$
F	$A_2 + T_1 + T_2$	$A_{2g} + T_{1g} + T_{2g}$
G	$A_1 + E + T_1 + T_2$	$A_{1g} + E_g + T_{1g} + T_{2g}$
Н	$\mathbf{E} + \mathbf{T}_1 + \mathbf{T}_1 + \mathbf{T}_2$	$\mathbf{E}_g + \mathbf{T}_{1g} + \mathbf{T}_{1g} + \mathbf{T}_{2g}$
Ι	$A_1 + A_2 + E + T_1 + T_2 + T_2$	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Table 4.2: Crystal field states in octahedral and tetrahedral coordination arising from free ion spectroscopic terms of a transition metal, from Burns (1993).

Т	L*	a^*	b*
		Mol1	
$25^{\circ}\mathrm{C}$	92.28	5.84	9.15
$100^{\circ}\mathrm{C}$	92.21	5.94	9.46
$200^{\circ}\mathrm{C}$	92.14	6.01	9.88
$300^{\circ}\mathrm{C}$	91.88	6.03	10.43
$400^{\circ}\mathrm{C}$	91.91	6.10	10.90
$500^{\circ}\mathrm{C}$	91.94	6.07	11.48
$600^{\circ}\mathrm{C}$	91.90	6.04	12.31
500°C, return	92.11	6.08	11.54
$200^{\circ}C$, return	92.41	6.08	10.11
$25^{\circ}C$, return	92.28	5.84	9.15
		TekCh1	
$25^{\circ}\mathrm{C}$	66.88	5.76	36.88
$100^{\circ}\mathrm{C}$	66.62	6.14	37.52
$200^{\circ}\mathrm{C}$	66.13	6.69	38.40
$300^{\circ}\mathrm{C}$	65.16	7.27	39.32
$400^{\circ}\mathrm{C}$	64.13	7.78	40.35
$500^{\circ}\mathrm{C}$	62.89	8.27	41.59
$600^{\circ}\mathrm{C}$	61.09	9.00	43.01
500° C, return	61.98	8.63	42.07
$200^{\circ}C$, return	65.07	7.01	39.21
$25^{\circ}C$, return	66.88	5.76	36.88

Table 4.3: L*a*b* coefficients of the textites samples between 25°C and 600°C.

Т	L*	a^*	b*
		MonoE51	
$25^{\circ}\mathrm{C}$	82.90	7.93	6.41
$100^{\circ}\mathrm{C}$	83.25	7.91	6.81
$200^{\circ}\mathrm{C}$	83.61	7.80	7.23
$300^{\circ}\mathrm{C}$	83.69	7.66	7.72
$400^{\circ}\mathrm{C}$	83.84	7.54	8.07
$500^{\circ}\mathrm{C}$	84.03	7.42	8.56
$600^{\circ}\mathrm{C}$	84.55	7.24	9.15
500°C, return	84.49	7.43	8.55
200°C, return	83.88	7.82	7.35
$25^{\circ}C$, return	82.90	7.93	6.41
		NM2	
$25^{\circ}\mathrm{C}$	85.34	8.97	9.88
$100^{\circ}\mathrm{C}$	85.60	8.74	10.50
$200^{\circ}\mathrm{C}$	85.90	8.50	11.06
$300^{\circ}\mathrm{C}$	85.84	8.22	11.52
$400^{\circ}\mathrm{C}$	85.81	7.93	12.04
$500^{\circ}\mathrm{C}$	85.78	7.56	12.84
$600^{\circ}\mathrm{C}$	85.90	7.13	13.97
500° C, return	86.05	7.62	12.79
$200^{\circ}C$, return	86.19	8.47	11.08
$25^{\circ}C$, return	85.34	8.97	9.88
		MarCoch2	
$25^{\circ}\mathrm{C}$	94.08	9.03	8.40
$100^{\circ}\mathrm{C}$	94.43	8.83	8.84
$200^{\circ}\mathrm{C}$	94.74	8.60	9.35
$300^{\circ}\mathrm{C}$	94.88	8.38	9.84
$400^{\circ}\mathrm{C}$	94.86	8.17	10.36
$500^{\circ}\mathrm{C}$	94.83	7.84	11.10
$600^{\circ}\mathrm{C}$	95.00	7.41	12.13
500° C, return	95.15	7.85	11.04
$200^{\circ}C$, return	95.01	8.59	9.32
$25^{\circ}C$, return	94.08	9.03	8.40

Т	L*	a^*	b*
		Lip4	
$25^{\circ}\mathrm{C}$	65.97	7.11	8.33
$100^{\circ}\mathrm{C}$	66.48	6.94	9.16
$200^{\circ}\mathrm{C}$	66.91	6.66	10.01
$300^{\circ}\mathrm{C}$	66.98	6.39	10.83
$400^{\circ}\mathrm{C}$	67.17	6.11	11.80
$500^{\circ}\mathrm{C}$	67.29	5.76	13.07
$600^{\circ}\mathrm{C}$	67.21	5.45	14.74
500° C, return	66.93	5.86	13.24
$200^{\circ}C$, return	66.35	6.70	10.17
$25^{\circ}C$, return	65.97	7.11	8.33
		Ecu1	
$25^{\circ}\mathrm{C}$	92.65	9.44	9.91
$100^{\circ}\mathrm{C}$	93.12	9.13	10.71
$200^{\circ}\mathrm{C}$	93.50	8.68	11.77
$300^{\circ}\mathrm{C}$	93.35	8.15	13.00
$400^{\circ}\mathrm{C}$	93.82	7.66	14.30
$500^{\circ}\mathrm{C}$	94.01	7.28	15.42
$600^{\circ}\mathrm{C}$	94.26	7.16	15.64
500° C, return	94.14	7.95	13.56
$200^{\circ}C$, return	93.40	9.32	10.63
25° C, return	92.65	9.44	9.91

Table 4.4: L*a*b* coefficients of the obsidian samples between 25 $^\circ\mathrm{C}$ and 600 $^\circ\mathrm{C}.$