

# *EUG XI*



Symposium PCM3

Glasses in Geosciences and in  
Environmental Sciences

Convenors

Laurence Galoisy  
B. Champagnon

Wednesday PO Session

**PCM3 : WEpo01 : PO  
Perlite Occurrence from a Columnary Jointed  
Rhyodacitic Lava, Ankara, Turkey:  
Preliminary Results**

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Perlite is a secondary product derived from the hydration of volcanic glasses. The term hydration here defines the diffusion of water into the volcanic glass, accompanied by a volume increase (McPhie et al., 1993). The perlitic occurrences of the investigated area, situated in 40 km NE of Ankara, were developed on a columnary jointed rhyodacitic lava flow. Its thickness reaches to 25 meters. The column diameters show progressive decrease from base to top of the outcrops (30-40 cm in diameter at the base with tetragonal polygon shape and 5-10 cm in diameter at the top with pentagonal and hexagonal polygon shape). Glassy texture is dominant in all parts of the columns.

Basal part of the columns have less contact with surface water and contains no perlitic formation, while middle and upper parts of the columns gradually show initiation of nucleation and growth of perlitic fractures. At upper part of the columns, grain size of perlitic increases, they are sometimes as large as "macro perlitic". The most upper part of the outcrops is covered with a 1-2 m thick clayey alteration zone. In this part, perlitic fines are well conserved with sizes up to 6 cm. We believe that the columnar joints allow the penetration of the alkali-rich surface water causing the hydration process and then perlitisation as a result. The source of alkali rich water is probably the evaporitic rocks present in studied area.

McPhie J, Doyle M & Allen R, *Volcanic Textures: A guide to the interpretation of textures in volcanic rocks. CODES (Centre for Ore Deposits and Exploration Studies, University of Tasmania) publications. 197pg, (1993).*

**PCM3 : WEpo02 : PO  
Study of Altered Volcanic Glasses from Iceland:  
The Protective Role of Zeolites and Gel Layer  
during Glass Corrosion**

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Subglacial basaltic hyaloclastites from the Vatnajökull area, in Iceland, were studied to approach the long term behaviour of natural glasses. These glasses, whose age lies between 3 and 4 My, altered by meteoric and sub-glacial waters, are surrounded by complex alteration layers.

The main alteration product is made up of massive zeolites (mainly chabazite, phillipsite and analcime) that could constitute 40% of alteration layers in volume. These zeolites are sometimes combined with others mineral phases (calcite or opal), but systematically associated with a microporous and amorphous gel layer in direct contact with the fresh glass. Mercury and water porosity measurements show that zeolites layer constitute a porous cement made up of a network of micro-channels less than 5 Angstroms.

An estimation of the glass dissolution rate has been made on the basis of the thickness of alteration layers. One can conclude that both zeolites and gel play a physical role in the kinetics of glass dissolution by forming a protective barrier capable of slowing down the alteration process from 130 µm/1000years (initial experimental rate) to 0,05 µm/1000years (final estimated rate).

The gel results from a double mechanism of hydration and hydrolysis of the initial glass. Moreover, zeolites lead to a selective dissolution of volcanic glass (which replace the initial congruent dissolution observed for younger samples) due to a cation exchange process occurring in their microporosity. This mechanism provokes a preferential leaching of some glass components, mainly Na and Ca, and its hydration.  $\delta^{18}O$  measurements indicate low temperature conditions (<20°C) and also attest a major modification of the initial glass structure during hydrolysis process and formation of the gel layer.

In conclusion, the formation of zeolites in natural environment does not imply a resumption of glass corrosion as previously observed during experiments by several authors for nuclear waste glasses. In contrary, they constitute with the gel layer a protective screen which slow down the glass corrosion and change the glass alteration mechanism.

**PCM3 : WEpo03 : PO  
Correlation between REE and Si Contents of  
Smectites, Formed by Alteration of Basaltic  
Glasses**

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Basaltic glass is investigated as a natural analogue for high level radioactive waste glass. Samples of hyaloclastites from the Vatnajökull area in Iceland from 3 to 4 million years old were studied [1,2]. The secondary phases formed by alteration of glass are mainly a hydrated gel layer covered by well developed tri-octahedral smectites, zeolites and calcite.

Nine smectite samples from three hyaloclastite series were separated and analysed for major elements by ICP-AES. The smectites differ with respect to the Si occupancy of the tetrahedral sites in the T-O-T layer. With respect to the formula of tri-octahedral or di-octahedral smectites ( $M_y R^{2+}_{3-y} R^{3+}_y (Si,Al)_6(OH)_2$ ) the Si value of the samples varies between 3,1 and 3,75. It is remarkable that the two samples from the youngest and therefore least altered hyaloclastite series have the lowest Si values. Crovisier et al. [3] calculated the chemical composition of the smectites formed during progressive dissolution of basaltic glass in meteoric water at equilibrium with the alteration products. They found that the smectites formed during progressive glass dissolution are increasingly enriched in Si. We therefore consider the Si values of the smectites as an indicator of the reaction progress.

The REE content of the smectite and of the residual unaltered glass was measured by ICP-MS. We find 3 to 12 ppm La and 0.1 to 0.5 ppm Lu in smectites whereas the glasses contain 8 to 10 ppm La and 0.4 to 0.5 ppm Lu. The REE values of smectites were normalised to the REE values of the corresponding glass. These normalised REE contents of smectites show a high correlation with their Si contents: with progressive glass dissolution the Si content of the smectites increases and the amount of REE taken up from the aqueous solution decreases. We conclude that the uptake of REE in smectites depends on the charge of the (Si,Al)O<sub>4</sub> tetrahedrons. The smectites are richer in LREE than in HREE. Smectites with a Si value of 3.1 contain 1.4 times more La and 1.1 times more Lu than the original glass. But smectites with a Si value of 3.75 contain only 0.4 times the amount of La and 0.3 times the amount of Lu in glass. The retention potential of smectite for REE decreases with increasing reaction progress. We assume that no HREE or LREE are taken up any more by smectites in the aqueous solution when all tetrahedral sites are occupied by Si.

Le Gal X, *These, Univ. Louis Pasteur, Strasbourg*, 128 p, (1999).  
Le Gal X, Crovisier JL, Gauthier-Lafaye F, Honnorez J & Grambow B, *C. R. Acad. Sci. Paris*, **329**, 175-181, (1999).  
Crovisier JL, Honnorez J, Fritz B & Petit JC, *Appl. Geoch. S.I.1*, 55-81

**PCM3 : WEpo04 : PO  
The Eutectic System Anorthite-Diopside:  
Thermal Expansivities of Supercooled Liquids  
Derived by Container-Based Dilatometry**

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Knowledge of the volume (density)-temperature relationship of silicate melts is essential for the modelling of melt transport and emplacement. In addition, establishing their volume equation of state requires accurate determination of thermal expansivities over a wide temperature range. Extrapolating expansivity data derived by Archimedean-

based stable liquid density determination to temperatures far below their calibration may be considered problematic since recent work on thermal expansivities of supercooled liquids allow to infer a nonlinear volume-temperature relationship over a wide temperature range from glass transition to stable liquid temperatures (Knoche et al., 1992; Gottsmann and Dingwell, 2000; Toplis and Richet, 2000).

Direct determination of thermal expansivities using dilatometry to derive the of supercooled silicate liquids is usually restricted due to the gravitational sample collapse at temperatures above the glass transition. Applying container-based dilatometry (Gottsmann et al., 1999) allows to benefit from this collapse as the sample is confined by a metal container during the course of the experiment. It is hence possible to directly determine the sample expansivity over a substantial temperature interval within the supercooled liquid field.

We have been investigating thermal expansivities of the 1 bar eutectic system anorthite-diopside over temperature ranges of up to 170 K. Combining supercooled diopside liquid expansivity data with stable liquid data gives the impression of a negative temperature-dependence of thermal expansivity, where the thermal expansivity decreases about 65% from metastable to stable liquid conditions. Supercooled liquid expansivity of the 1 bar eutectic composition anorthite-diopside decreases from 0.0008824 cm<sup>3</sup>/mol K between 804 and 940°C to 0.0007273 cm<sup>3</sup>/mol K between 940 and 973°C, displaying a smooth negative temperature dependence over the investigated temperature range. Preliminary results on anorthite doped with small amounts (about 2 wt%) of diopside component give a coefficient of thermal volume expansion of 0.0000056 /K for the temperature range 857 to 947°C consistent with results from dilatometrical investigations at similar temperatures (Knoche et al., 1992; Toplis and Richet, 2000).

The data obtained by container-based dilatometry reveal a constant increase of coefficients of thermal volume expansion with increasing diopside content within the investigated system, a behaviour similar to what was proposed by Knoche et al.(1992).

Gottsmann J & Dingwell DB, *Contrib. Min. Pet.*, **139**, 127-135, (2000).  
Gottsmann J, Dingwell DB & Gennaro C, *Am. Mineral.*, **84**, 1176-1180, (1999).  
Knoche R, Webb SL & Dingwell, DB, *Geochim. Cosmochim. Acta*, **56**, 689-699, (1992).  
Toplis MJ & Richet P, *Contrib. Min. Pet.*, **139**, 672-683, (2000).

**PCM3 : WEpo05 : PO  
Volumetric Properties of Halogens-Bearing  
Silicate Glasses**

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The presence of halogens dissolved in natural magmas is of great interest for a wide variety of reasons. Halogens influence the physico-chemical properties and the structure of silicate glasses and melts, their phase relations, and as a consequence play a significant role in the petrogenetic processes occurring in the Earth's interior. In addition volcanic emissions of halogens may influence climate.

In order to address the role that halogens play in the physico-chemical properties of silicate glasses, volumetric measurements have been conducted on halogens (F, Cl, Br and I) containing Fe-sodium disilicate glasses. Experimental investigations were performed at room-temperature using Archimedean method to the glass transition temperature using a push-rod dilatometer. Starting compositions were a series of glasses synthesized by the addition of FeF<sub>3</sub>, FeCl<sub>3</sub>, FeBr<sub>3</sub> and FeI<sub>3</sub> to sodium disilicate. Halogens contents range from 0 to 4, 3, 4.5 and 1.5 wt%, respectively for F, Cl, Br and I.

The oxidation state of the present glasses was investigated using <sup>57</sup>Fe Mössbauer spectroscopy and varies from almost completely oxidised (i.e., F- and Cl-containing glasses) to samples containing approximately 57% of Fe<sup>3+</sup> (i.e., I-containing glasses), whereas the oxidation state increases with increasing Br-content for Br-containing glasses.

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Preliminary density measurements at room-temperature of these glasses suggest an increase of density with increasing halogens and iron contents. In addition, analyses of the present results may indicate a negative effect of Cl on the density of Fe-containing sodium disilicate glasses and an opposite effect for F. Further investigations on the present glasses of the volumetric behaviour at higher temperature are still in progress.

### PCM3 : WEpo06 : PO Configurational Entropies of Silicate Liquids and Phase Diagrams

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To arrive at a better understanding of the structure-property relationship, high-viscosity measurements and heats of dissolution of silicates have been performed in the system  $\text{SiO}_2\text{-Na}_2\text{O}$ . This simple system is made up of just a network former plus a network modifier and has a great industrial and geological interest.

Along with ancillary data, these measurements have been used to determine the configurational entropy of melts along these joins with the Adam-Gibbs theory. As the configurational entropy is a good probe of the structure of the liquid, the implications of this work will be discussed in terms of chemical and topological entropy.

The implications for Gibbs free energies and the miscibility gap will also be discussed.

Finally, we will describe a calculation of the phase diagram with no adjustable parameter, using only thermodynamic and configurational entropy data.

### PCM3 : WEpo07 : PO The Structure and Characteristics of Fulgurite Glasses

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Fulgurites is a glassware tubular bodies, which formed after the melting of rocks by the hit of a lightning. They are relatively rare and not enough studied geological objects. In our investigations we use several methods such as: X-Ray analysis, Mossbauer spectroscopy, infra-red spectroscopy, electronic microscopy. We studied fulgurite from the area of Nigoziro in Karelia, Russia, which formed on a carbon-containing aleurolites. The main component of fulgurite is aluminosilicate glass, which chemical composition is rather correspondent to the composition of carbon-bearing aleurolites. With the help of X-Ray analysis we find that fulgurite glasses have quartzo-felsphatic composition. Also we expose the heterogeneity of glasses which consists in combined presence of amorphous glassy matrix and crystalline formations with differ composition: orthoclase, hematite, chlorite, pyrite. The state of iron in fulgurite was studied with the help of Mossbauer spectroscopy. In spectrum distinguished fore double-peaks of iron. One double-peak of trivalent iron in tetrahedral position ( $d = 0.32$ ), which contains 4.1% of all iron, and three double-peaks of divalent iron in octahedral positions. The last differs by extent distortion of octahedrons ( $d = 1.1; 1.13; 1.05$ ). The content of iron at that positions accordingly 33.9; 30.4; 31.6% from all amount of iron. The ratio of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  in sample makes up 23.4%. The infra-red spectrums of fulgurites consists from the typical for the silicate glasses absorption stripes, which connected with the oscillation of silicium-oxygen carcass of glassy fulgurite substance. Also we find several narrow stripes of crystalline quartz which is an evidence of crystalline quartz presence in felsphatic fusion. By the micro-probe analysis we determined that the main mass of glassy fulgurite substance is a thicken Si-Al-Fe fusion. In the main mass of fusion the areas of almost pure glasses are distinguished. The simultaneous appearance of fragments as glassy such as residual quartz in fusion tells that the temperature of fusion in that zone was near the temperature of quartz melting, this is about 1700°C. In the outlying districts of fulgurite iron contains by the higher portions. Here we find a great amount inclusions, mainly of Fe-Al composition. In the fulgurite glass we also find an inclusions of almost pure alloy which consists from the iron and aluminum with the small admixture of magnesia. That inclusions are characterized by the good crystallographic cutting. The presence of costal

growing forms tells about the post-melting formation of this inclusions. Also we often meet inclusions of hematite  $\text{Fe}_2\text{O}_3$ . His grains have the straight borders. The appearance of this inclusions allow as to estimate the temperature of the fusion which did not reach the temperature of hematite melting. Besides, in the glass, we find the inclusions of hematite with the tracks of partial fusion. Appearance of a great amount skeleton formations with the composition such as FeO (wüstite) is an evidence of a great fusion cooling speed. Such structures forms because of dissociation on the cooling stage. Also the cleaning of glass from the admixture iron happening.

### PCM3 : WEpo08 : PO Properties and Structure of Calcium Aluminosilicate Glasses and Melts

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Calcium aluminosilicate glasses are attractive materials for a wide range of technical applications due to their highly refractory nature, their excellent optical and mechanical properties. The  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system (CAS) is remarkable since glasses with very few  $\text{SiO}_2$  content can be synthesized, contrary to alkali or Mg aluminosilicate glasses. We have synthesised more than 40 different chemical compositions. Thermodynamic and rheological properties were studied using calorimetric and viscosimetric measurements. The glass ans melts structure were investigated using various methods: X-ray and neutrons diffraction, Raman spectrometry, X-ray absorption spectroscopy at Si, Al, Ca K edges. These techniques allowed the determination of the local and medium range environment. From all these studies we can show that:  
- Al is in tetrahedral site in all the CAS system.  
- Ca is in octahedral site in all the CAS system, with a decrease of the site distortion with increasing  $\text{SiO}_2$  content.  
- The anomalous behaviour for the viscosity and glass transition properties in the low silica glasses can be explained by the presence of Al in Q3 species.

### PCM3 : WEpo09 : PO Internal Friction Spectroscopy in $\text{Li}_2\text{O-2SiO}_2$ Partially Crystallised Glasses

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Shear modulus and internal friction measurements were conducted on disilicate lithium glasses  $\text{Li}_2\text{O} - 2\text{SiO}_2$  on samples containing 0, 17, 22 and 27 vol.% of crystals. The  $\text{Li}_2\text{Si}_2\text{O}_5$  glass without crystals has  $T_g \sim 470^\circ\text{C}$ . By varying temperature and duration of annealing a different volumetric content of disilicate lithium crystals may be generated, because nucleation and crystal growth peak temperatures do not overlap (Brückner et al., 1993). Shear modulus and internal friction spectroscopy were carried out by the use of torsion oscillatory shear apparatus in a frequency range 20-0.002 Hz and temperature range 350-490°C (Bagdassarov, 2000). Glassy samples represented cylinders 8 mm in diameter and 25 mm in length. Data obtained at different frequencies and temperatures were reduced to master curves by the use of frequency normalisation to shear stress relaxation times measured at low frequencies and high temperatures, where samples behave as Newtonian liquids. Relaxation times for samples 0, 17, 22 and 27 vol.% of crystals relate as 1 : 3 : 4 : 5.5. Activation energies of relaxation times for tested samples are 456 (0%), 436(17%), 420 (22%), and 367(27%) kJ/mol. There is small (c. 10%) increase in the unrelaxed shear modulus of glass with the crystal content increase from 0 to 27 vol.%. At high frequencies and low temperatures ( $Q^{-1} < 0.05$ ) complex shear modulus and internal friction follow Kronig-Kramer relations. Frequency dependence of the internal friction  $Q^{-1} \sim 1/\omega^{0.45}$ . Master curves of glasses with differing crystal contents do not fit Maxwell relaxation model. Peaks of imaginary component of shear modulus

are asymmetric with an extended high frequency-low temperature shoulder, peaks are broader than Debye peak, covering c. 4 decades of normalised frequency.

Bagdassarov N, In: *Physics and Chemistry of Partially Molten Rocks* (eds. Bagdassarov N, Laporte D, Thompson A), Kluwer Academic Publisher, 29-66, (2000).

Brückner R, Deubener J, Sternitzke M, *J Non-crystalline Solids*, 163, 1-12, (1993).

### PCM3 : WEpo10 : PO Environment of Nickel, Cobalt, Zinc in Alkali Borate Glasses: Information from EXAFS and XANES Spectra

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Nickel and cobalt are known to be efficient coloring agents in glasses. Ni-bearing, low alkali borate glasses exhibit colors ranging from green to yellow, which were related to the presence of six fold-coordinated Ni according to optical absorption spectroscopy and EXAFS data. Peculiar NiO clusters were recently evidenced in these glasses, despite a high dilution level. Ni-O and Ni-Ni distances are consistent with a Ni surrounding which mimics a NiO local structure. MS paths are responsible for the observation of a feature along distance which is due to a focusing effect involving three nearly colinear NiO<sub>6</sub> octahedra. Structural features characteristic of NiO are absent in the borate glasses showing that these Ni-containing ordered domains do not correspond to unreacted NiO crystallites. This explains the low NiO activity in alkali borate glasses as the Ni enriched domains may lead to the formation of nucleation centers precursors of NiO crystallites. Similar EXAFS spectra were obtained at the Co and Zn K edges in potassium borate glasses showing the peculiar MS feature at 6Å. This indicates the presence of clusters which mimic a cubic close packed structure. The significance of these oxide clusters will be discussed. When the alkali content increases up, the local environment is modified with the Ni coordination decreasing towards the high alkali content. Similar observations are made for cobalt bearing alkali borate glasses. The coordination of both transition elements were investigated using high resolution XANES spectra (pre-edges) and allow to evidence a modification of coordination with increasing alkali content. These changes are related to the structural modifications of the glass with increasing alkali content.

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## Glasses in Geosciences and in Environmental Sciences

### Thursday PM Session

#### PCM3 : THpm22 : G6 Neutron and X-Ray Diffraction Studies of the Structure of Glasses and Liquids

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The determination of the structure of oxide glasses and liquids is of great importance in various domains such as geophysics, material and environmental science, in order to understand their physical properties (density, viscosity ...). This talk will review some recent studies obtained on silicate and borosilicate glasses from a combination of neutron and X-ray diffraction methods, exploiting the different contrast for the two types of radiation. In addition, Molecular Dynamics models coupled with the Reverse Monte Carlo technique can help to extract structural information from the experimental data. The complementary use of diffraction and modeling techniques allow to probe both the polymerization of the network and the structural role of the non-network forming elements, such as Na and Ca. In particular, the environment around Na and Ca can be different either they act as charge compensator or modifier into the glass structure. Furthermore, these techniques can now be applied to the liquid state in order to shed light on the possible structural differences between the glass and the liquid. Structural modifications appears to be continuous with increasing temperature and the local cationic environment is few affected. Apart the expected thermal broadening, important structural differences are discernible at the medium range scale between the diffraction data at high temperature (liquid state) and those of the glass at ambient temperature.

#### PCM3 : THpm23 : G6 Raman Spectroscopic Investigations of High Temperature Configurational Changes in Silicate Melts

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In the last twenty years, there have been considerable efforts in the development of various techniques allowing to study the physical properties of silicate glasses and liquids and their relationship with the short to medium range structure. In particular, considerable progress has been made to allow structural characterization in the liquid field (i. e. at temperatures higher than the glass transition). We discuss here the input from Raman spectroscopy, which is shown to be a versatile technique that allows to study in situ geologically relevant silicate liquids at high temperatures (HT) (1000 to 2000K). These data can be used to provide information on:

- 1) the general structure of the aluminosilicate network and its evolution with temperature
- 2) configurational changes affecting peculiar molecular units when the melt chemistry is complexified with the addition of high field strength elements at the percent level
- 3) liquid-liquid immiscibility and kinetics of unmixing. Various examples taken from studies carried out in our laboratory are used to illustrate progresses in the interpretation of HT Raman spectra and critical examination of the advantages and shortcomings of Raman spectroscopy with respect to other spectroscopies will be given.

#### PCM3 : THpm24 : G6 Titanosilicate Glasses Studied by Solid-State NMR Spectroscopy

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Titanosilicate glasses are of interest both technologically and geochemically. Due to the addition of Ti significant changes in the density, compressibility and thermal expansion have been reported. Furthermore, there are anomalous

changes in heat capacity just above  $T_g$  when compared with binary silicate melts. These changes in  $C_p$  must be associated with significant structural changes. Oxygen-NMR (Nuclear Magnetic Resonance) is an attractive method to resolve this issue as it provides information about the distribution of oxygen environments. Configurational changes in the melt will be reflected in this distribution of oxygen environments (e.g. Si-O-Si, Si-O-Ti, K-O-Si). As a preliminary step to high temperature NMR studies of the melts themselves we have characterised the distribution of oxygen environments in the glasses. Three glasses have been included in this analysis :  $K_2O.TiO_2.2SiO_2$  (KTS2),  $K_2O.3SiO_2$  (KS3), and  $Na_2O.TiO_2.2SiO_2$  (NTS2) by which the influence of the various components in the glass is explored. Oxygen sites in the spectra have been assigned and their relative amounts determined. Using this information a model for the glass based on the oxygen network is proposed.

#### PCM3 : THpm25 : G6 Hydrofluoric Acid Solution Calorimetric Data for Sodium Silicate Glasses: Support for Configurational Entropies from Adam-Gibbs Theory

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Within the framework of the Adam-Gibbs theory of structural relaxation, viscosity and heat capacity data may be combined to determine configurational entropies of silicate glasses. When applied to binary sodium silicate glasses ( $Na_2O-SiO_2$ ), positive entropies of mixing ( $S_{mix}$ ) are calculated for compositions between 0 and 30 mole%  $Na_2O$ , a compositional range where liquid immiscibility is known to occur and where values of Gibbs free energies of mixing ( $G_{mix}$ ), therefore, must be positive. Because positive entropies of mixing contribute negatively ( $-TS_{mix}$ ) to  $G_{mix}$ , the observed immiscibility requires positive enthalpies of mixing ( $H_{mix}$ ) in this compositional range. In order to test this inference, and indirectly check the validity of entropies calculated using the Adam-Gibbs modeling technique, we have made HF solution calorimetric measurements on a series of sodium silicate glasses.

Glasses for this study were synthesized at ten compositions ranging from pure silica to 50 mole%  $Na_2O$ . Fictive temperatures are well known for all but one glass. Solution calorimetric measurements were conducted under isoperibolic conditions in 20.1 weight% HF at all compositions. These relatively low-temperature solution calorimetric measurements (50°C) assured that the glasses did not change state during the dissolution experiments. Raw heats of solution were corrected to those of a common fictive temperature based on known glass and liquid heat capacities (Richet et al., 1982).

Despite the hygroscopic character of the more sodic samples, the calorimetric results were highly reproducible, having an average spread of 0.3% of the heats of solution (about 0.5 kJ/gfw). This is small relative to the 35 kJ/gfw (where one gram formula weight is based on a single mole of oxides) variability in enthalpy of solution among the various glasses. When plotted against composition, the negatives of the enthalpies of solution display a well-defined concave-down curve for samples having compositions between 0 and 40 mole%  $Na_2O$ , as well as a sharp energy well near 40 mole%  $Na_2O$ . The resulting positive enthalpies of mixing in the 0-40% compositional region correlate well with the positive Gibbs energies of mixing and the liquid immiscibility in this region. These calorimetric results give further strong support to the usefulness of Adam-Gibbs theory for the prediction of viscosity/entropy behavior of silicate glasses and liquids.

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*Geochim. Cosmochim. Acta*, **46**, 2639-2658, (1982).

#### PCM3 : THpm28 : G6 Assessing Ancient Glass-Technology by Microanalyses

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The reconstruction of the whole glass-melting process in archaeology allows advancement of knowledge on ancient material culture. Up to now, archaeometric investigations are mainly devoted to decipher the provenance attributes using bulk chemical characters. This implies the assumption of an homogeneous composition of glasses. Studies on the glass heterogeneities and on the close relationships existing between microtextures and micro-chemistry are still poorly established. We present here preliminary analytical results of coupled microtextural and microchemical analyses of historic glassy materials in order to understand the production processes and to reconstruct some technological expedients used to produce glasses, in ancient times. Several examples taken from vitreous masses and worked glasses reveal textural and chemical evidences of compositional un-homogeneities: i) melt immiscibility are testified by separation of gas (bubbles) and metallic phases (iron-phosphide) and compositional variations related to different viscosity. Following the Zachariasen's (1932) theory, the polymerisation pattern of glasses and its viscosity is directly related to the ratio between network-formers and network-modifiers cations, that correspond to vitrifying ( $SiO_2$ ,  $Al_2O_3$ ) and stabilising/flushing (CaO, MgO, FeO /  $K_2O$ ,  $Na_2O$ ) components, respectively. Compositional changes through a glass are common and produce an heterogeneous mixture containing discrete portions of the end-member glasses and consequently chemical un-homogeneity that can be interpreted in terms of batch components. ii) the presence of zoned clinopyroxene provides new insight into crystallisation dynamics occurring in melted glass masses. Even if the FeO/MgO ratio increases from core to the rim, according to a normal crystallisation path, oscillatory zonings testify the scarce diffusion within the melt during diopside crystallisation and an alternate concentration of rejected solute as crystallisation proceeds. Phase crystallisation is ruled by undercooling rate of melted glass. Crystal growth is controlled by the rate of transport of fusion heat away from interface. In this situation systems typically exhibit dendritic or spherulitic morphologies. Textural and chemical un-homogeneities within ancient glasses can be revealed and interpreted using a methodological approach, commonly used in the petrology studies. This leads to the definition of "production indicators" that help to reconstruct some technological aspect of ancient glass making.

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#### PCM3 : THpm29 : G6 Measuring the Ratios of Ferric to Ferrous Iron in Glasses with the Electron Microprobe

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The precision of the method is strongly dependent on the total Fe concentration. For basaltic glasses (with 8 wt% Fe as average value) the precision of the method is about  $\pm 2\%$  absolute. The technique is applicable to silicates and glasses with total Fe concentration above 3.5 wt%.

The technique has been applied to the study of a thin section of komatiitic lavas in which  $Fe^{3+}/\Sigma Fe$  has been measured from micrometer-sized areas of glasses (10-20  $\mu m$ ) either present in the matrix of clinopyroxenes and devitrified glasses or trapped as inclusions in serpentinized olivines. This study has revealed in particular the high sensitivity of glassy matrix to electron beams. Common discrepancies observed are related to oxidation under the high beam currents leading to overestimated  $Fe^{3+}/\Sigma Fe$ . Protocols have been carried out to correct raw data for these oxidation kinetics. The redox state of Earth's mantle is a critical parameter to constrain models on the origin and evolution of the Earth. Oxygen fugacity plays an important role in volatile speciation, physical properties of mantle rocks, core-mantle interactions, and the atmosphere chemistry through time. The redox state of the upper mantle is commonly estimated through values of oxygen fugacity

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calculated on the basis of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  equilibrium among mineral assemblages such as olivine-orthopyroxene-spinel or determined by wet chemistry on minerals or glasses. The effect of different processes on the mantle redox conditions are still debated: are the large variations in the redox state linked to C-O-H fluids or result only from magmatic processes, partial melting and melt infiltration? Many of the controversies about this subject ultimately relate to the sparsity and non-relevance of the data available. That may be the major justification for continuing to search for techniques of determining  $\text{Fe}^{3+}/\Sigma\text{Fe}$ . Different microbeam methods are commonly used to measure  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in silicates and glasses. Among them, a method based on the relationship between the self-absorption induced shift of the Fe L $\alpha$  peak maximum, as measured with the electron microprobe, and the oxidation state of iron has been recently developed (Fialin & Wagner, 1999; Fialin et al., 2000a; Fialin et al., 2000b; Fialin et al., in press). Results for  $\text{Fe}^{3+}/\Sigma\text{Fe}$  are deduced by comparison of raw data.

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### PCM3 : THpm30 : G6 The Thermal History of a Pantelleritic Lava Flow: The 8-ka Fountain-Fed Obsidian Flow on Mayor Island, New Zealand

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Relaxation geospeedometry using differential scanning calorimetry (DSC) has been applied to focus on the thermal history of a 8000 year old fountain-fed obsidian flow on Mayor Island, New Zealand. This method is based on the quantification of the relaxation of enthalpy upon reheating natural obsidians across their glass transition and allows to model the natural volcanic cooling rate associated with the transition from the supercooled liquid to the glass.

The clastogenic pantelleritic flow overlies syn-eruptive loose pumice-fall deposits and exhibits an up to 40 m thick crystalline core sandwiched in between two obsidian layers: a <1 m thick lower obsidian (LOBS) and an in average 5 m thick folded upper obsidian (UOBS) overlain by a vesicular flow carapace.

The LOBS has been investigated in a vertical profile where the flow drapes the steep inner walls of a caldera. The UOBS was sampled along a horizontal 30 m wide profile on a wave-cut platform at the eastern shoreline of the island. Cooling rates for the LOBS decrease from about 0.04 K/hour directly adjacent to the crystalline core to 1K/hour at the basal contact to the pumice deposit. The modelled cooling data for the spine-like obsidian ridges of the UOBS in average show variations between 0.1 K/hour and 0.7 K/hour. In addition, some ridges were quenched at significantly faster rates exceeding 350 K/hour.

The fast rates are interpreted to represent the cooling dynamics in flow ridges that during flowage deeply protrude into the vesicular carapace to surface near levels. In contrast cooling rates for obsidians directly or closely adjacent to the crystalline core show similar cooling rates in the order of few K/day. These slow cooling rates may result from a thermal process associated with stages of thermal annealing during flowage. Glassy material that may have experienced a primary fast quenching process may have successively been reheated to supercooled liquid conditions, e.g. during the incorporation of rapidly cooled disintegrated material of the flow front into the flow base upon flow advance. The higher temperatures of the flow interior in addition to the production of latent heat during the crystallisation of the core would account for a prominent heat source for reheating such material. This reheating seems to have been accompanied with an (quasi-) isothermal annealing interval resulting in a pronounced structural relaxation that can now be quantified by the very slow cooling rates modelled for the central parts of both obsidian layers. Processes responsible for such annealing regimes and possible temperature-time relationships at different

levels within the flow will be discussed as well as implications for flow mobility and hazard assessment of low-viscosity pantelleritic fountain activity.

### PCM3 : THpm31 : G6 New Insights into the Structural Environment of Fe in Synthetic and Natural Glasses, using an Improved Analysis of $^{57}\text{Fe}$ Mössbauer Spectra

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A set of synthetic Fe-bearing hydrous glasses with variable redox ratio (0% <math>\text{Fe}^{3+}/\text{Fe}\_{\text{tot}}</math> <math>< 40\%</math>) is used to illustrate what kind of structural information can be extracted from Mössbauer spectra analysed using methods especially dedicated to amorphous/disordered compounds. Indeed, Fe-Mössbauer spectra for amorphous compounds have long been analysed in a way similar to that used for crystals in which the intrasite distribution of Fe is often well defined. This assumption leads to a biased picture of the structural environment of iron in glasses, as these methods are based on a discrete spectral deconvolution.

The methods used in this study (see Rossano et al., 1999 for details) take into account a distribution in both isomer shift and quadrupole coupling, independently from each other. This is required to render both site distortions and coordination changes that occur for a continuous range of Fe sites.

Glasses (61 mol%  $\text{SiO}_2(\text{Qz})$  - 15.3 mol%  $\text{NaAlSi}_3\text{O}_8(\text{Ab})$  - 21.5 mol%  $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{An})$ ) contain 1.6 wt% of  $\text{Fe}_2\text{O}_3$  and 11 wt% of  $\text{H}_2\text{O}$ . They were synthesized under water saturated conditions at 500 MPa, 850°C and 950°C. The oxygen fugacity was varied in the  $f\text{O}_2$  range from Cu-Cu $_2\text{O}$  buffer to slightly more reducing conditions than the wüstite-magnetite buffer (Wilke and Behrens, 1999). A few experiments were performed to investigate the effect of quench rate on Fe speciation. In addition to experiments using the normal quench rate (decreasing from ca. 150K/min above 500°C to 100K/min below 500°C) runs were performed with slower and faster quench rate.

Using methods especially dedicated to amorphous compounds improve the quality of the data extracted from experimental spectra in a qualitative and quantitative way. First, the analysis of the Mössbauer parameter distribution allows a model-independent determination of iron redox ratio in silicate glasses. The values derived will be discussed and compared to the ones derived using classical deconvolution methods and x-ray absorption fine structure spectroscopy (pre-edge analysis). At constant redox ratio, major structural differences are observed between hydrous glasses synthesised with different quenching rates. Local ordering around Fe of the slowly quenched glass is related to the crystallisation of various Fe oxides, based on transmission electron microscopy and XAFS experiments. On the other hand, the Mössbauer information for the dry glass shows a distribution which is strongly different from its hydrous counterparts, evidencing the efficient ordering effect of water around transition elements in silicate glasses/melts. Finally, first applications of this method to derive information on iron in natural volcanic glasses (basalts and obsidians) will be presented.

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Wilke M & Behrens H, *Contrib Mineral Petrol*, 137, 102-114, (1999).

### PCM3 : THpm32 : G6 Effect of Leaching on Nuclear Glasses: A Spectroscopic Study

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The glass R7T7 is used for the storage of the nuclear wastes. It's a multicomponent borosilicate glass (about 30 elements). The inactive glass contains 0.85% of actinides and about 11% of homologues of fission's products. The purpose of this study is the evolution of the structure of glasses close to the inactive R7T7 after leaching.

Several spectroscopic methods are used: photoluminescence, cathodoluminescence, micro-Raman and micro-infrared. We study first some special glasses doped with rare earth. They present a special Raman spectra compared to other borosilicate glasses showing a band at 850  $\text{cm}^{-1}$  which may be attributed to crystallisation of nepheline (Li et al, 2000). The structure of the corresponding gel will be precised by micro-Raman and micro-Infrared. Using photoluminescence, we are principally interested in three component U, Cr and Eu. Eu and Cr are used as luminescent structural probes. Fluorescence Line Narrowing is used in order to precise the environment of the  $\text{Eu}^{3+}$  in the glass and in the corresponding gel, induced by leaching. In the glass the ion  $\text{Eu}^{3+}$  is surrounded by a borate environment where as the leaching glass shows a silicate one as it was reported from chemical analyses.

Two kinds of glasses containing U were studied, one containing Fe and the other not. Under laser excitation, the two glasses show a yellow luminescence characteristic of the uranyl ion  $\text{UO}_2^{2+}$  (U VI). In the two corresponding gels, the luminescence of uranyl is much weaker than in the glasses. Furthermore this emission is nearly quenched in the iron rich gel. SEM analyses and images revealed that U is concentrated in crystallized Ba-rich micro phases (15-20  $\mu\text{m}$ ) unlike in glass where it is distributed homogeneously.

In order to follow the charge valence and environment modification, in the complex glass, we synthesised Cr-doped simplified glasses : one borate, one borosilicate and one silicate. Each glass was studied by optical absorption, photoluminescence and EPR measurements.

Li H, Su Y, Vienna JD, Hrma P, *Journal of the American Ceramic Society*, (2000).

### PCM3 : THpm33 : G6 The Effect of $\text{P}_2\text{O}_5$ on the Ferric-Ferrous Ratio in Basaltic Liquids at Atmospheric Pressure

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Although the concentration of  $\text{P}_2\text{O}_5$  in natural magmas is generally low (less than 2-3 wt.%), P strongly modifies the liquidus phase relations and hence the differentiation trends of basaltic magmas (Kushiro, 1975). In particular, the stability field of magnetite is significantly reduced with increasing phosphorus content in a ferro-basaltic melt (Toplis et al. 1994). This could either be due to a decrease of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in the liquid or to the formation of stable P- $\text{Fe}^{3+}$  complexes in the melt which would inhibit the crystallization of magnetite.

We have conducted superliquidus experiments (1150-1190°C) at 1 bar to study the influence of phosphorus on the ferric-ferrous ratio of basaltic glasses. The starting materials were synthetic glass powders of ferro-basaltic and transitional alkalic composition with  $\text{P}_2\text{O}_5$  contents ranging from 0 to 4.4 wt.%. For each experiment, a small charge of starting material was sintered onto a loop of thin Pt-wire (pre-treated to minimize iron loss). The oxygen fugacities corresponding to FMQ+1 and FMQ-1 were controlled using  $\text{CO}/\text{CO}_2$  gas mixtures. The samples were equilibrated for 8 h and drop quenched into distilled water. The ferric-ferrous ratio of the quenched melts were determined with Mössbauer spectroscopy. The spectra show two broad absorption lines typical for reduced silicate glasses. They have been

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fitted with two quadrupole split doublets resulting from  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . For glasses equilibrated at FMQ+1,  $\text{Fe}^{3+}/\Sigma\text{Fe}$  strongly decrease from 0.37 to 0.27 with increasing  $\text{P}_2\text{O}_5$  content. At lower oxygen fugacities (FMQ-1)  $\text{Fe}^{3+}/\Sigma\text{Fe}$  remains constant at around 0.14.

The  $f\text{O}_2$  dependent influence of  $\text{P}_2\text{O}_5$  on the ferric-ferrous ratio seems to be related to the changing role of  $\text{Fe}^{3+}$  in the glass structure. Ferric iron is known to be tetrahedrally coordinated in oxidized, but octahedrally coordinated in reduced quenched silicate melts. In contrast,  $\text{Fe}^{2+}$  is independent of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  octahedrally coordinated. According to Virgo and Mysen (1985) the coordination transformation is indicated by an increase of the isomer shift for  $\text{Fe}^{3+}$  from 0.3 to 0.5 mm/s. In addition, the half widths in the component peaks of the  $\text{Fe}^{3+}$  doublet are largest (up to 1.09 mm/s) in the range of intermediate  $\text{Fe}^{3+}/\Sigma\text{Fe}$ . Indeed, with decreasing  $\text{Fe}^{3+}/\Sigma\text{Fe}$  we observe a small increase of the isomer shift (0.39 and 0.46 mm/s) and a decrease of the half width in the component peaks of the  $\text{Fe}^{3+}$  doublets (0.7 to 0.5 mm/s). Both features point to a decreasing amount of tetrahedrally coordinated  $\text{Fe}^{3+}$ . Phosphorus removes metal cations from the aluminosilicate network to form phosphate complexes outside the network. This results in the formation of more Si-O-Si bonds and hence in an increase in the polymerization which may lead to a reduction of tetrahedral ferric iron to octahedral ferrous iron.

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The work of Steinmann et al. (1999) shows a fractionation of the light rare earth elements in salts next to a Miocene basalt dyke, suggesting a very low mobility of certain radiotoxic elements (e.g. Am and Cm) in a radwaste salt repository.

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### PCM3 : THpm34 : G6 Are the Natural Analogues Really Useful?

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It is not possible to assess the long term performance of waste form glasses only by the predictions of models using parameters measured during short-term experiments. Moreover, numerous glass corrosion studies have revealed the complexity of the process by which alteration layers are formed on the glass surface. In this context, many people think that natural analogues are essential to extrapolate to the long term the results obtained at the laboratory and to test the validity of hypothesis and concepts. However natural analogues are often presented as materials or environments which have to resemble those under consideration for the storage of waste in natural environment. This too restrictive definition often led to ambiguities or disappointments in the last decade.

In some cases the study of natural sites effectively brings information almost directly transposable to the sites of storage (for example the measurement of chemical species migration). In other cases the natural analogues enable us to test assumptions or to question conclusions obtained by laboratory experiments (for example : which is the impact of zeolites formation on the evolution of the long term corrosion rate of the glass ?). In addition the study of natural sites makes it possible to evaluate the complexity of the phenomena and the multitude of parameters to be taken into account in the models. The sites of Oklo or Bangombé in Gabon are particularly teaching examples on this subject (Bracke et al., 2000, Gauthier-Lafaye et al., 2000). Finally, it is necessary to insist on the fact that the predictive models used for the glassy source-term are the fruit of works on crystalline rocks alteration.

The study of Le Gal et al. (1999) shows that the formation of a zeolites layer around the grains of volcanic glasses causes a change in the mechanism of glass alteration and a reduction of the corrosion rate whereas laboratory experiments lead to opposite conclusions.

The study by Techer (1999) of a superficially vitrified basaltic dyke from the Salagou (France) intruding in a pelite, shows that the corrosion rate of the glass is 100 to 1000 times weaker than the rate experimentally measured (Techer et al. 2000). These results encourage to moderate the conclusions of experimental works which highlighted a penalising effect of certain clays.