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#### Bulk solubility and speciation of $H_2O$ in silicate melts

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#### ABSTRACT

The bulk solubility and speciation of  $H_2O$  in silicate melts of virtually any composition is predicted from first principles with a satisfactory precision. The solubility of molecular water is first predicted from the Scaling Particle Theory (SPT) coupled with an *ab initio* assessment of the electronic, dispersive and repulsive energy terms based on the Polarized Continuum Model (PCM). The Silver-Stolper ideal homogeneous speciation model is then applied to compute the fractional molar amount of neutral hydroxyl functionals  $[OH]^{\circ}$  in the melt and the computed  $[OH]^{\circ}$  amount is added to the molecular form  $[OH_2]$ . The Hydrogen Bonding (HB) electrostatic contributions to the stabilization of molecular water  $[OH_2]$  in solution are then resolved through an inverse non-linear minimization procedure on the basis of an extended dataset (970 samples) of experiments concerning the H<sub>2</sub>O saturation hyper-surface carried out in the last half century. The Gibbs free energy of solution  $\Delta G_{s}$ , the  $\Delta G_{HB}$  contributions and the energy terms involved in the homogeneous speciation reaction are shown to be consistent with first principles. The procedure is fully predictive (i.e. no need of an initial hint about approximate bulk amounts of H<sub>2</sub>O in solution) and sufficiently accurate to be proposed as an exploratory tool (mean absolute accuracy of ~ 2.1 kJ/mole in terms of energy and ~1.7% in terms of fractional molar amount X<sub>H2O</sub> per unit mole of liquid).

#### **KEYWORDS**

### H<sub>2</sub>O solubility, Henry's Law, Silicate Melts, Hydrogen Bonding

### HIGHLIGHTS

- The H<sub>2</sub>O solubility in silicate melts is predicted with high accuracy through application of first principles.
- The role of Hydrogen Bonding in enhancing the solubility of molecular water is quantified.
- Pressure enhances dramatically the bulk H<sub>2</sub>O solubility in silicate melts.
- The thermal effect of bulk solubility is essentially determined by the Cavitation Energy.
- The dielectric constant and the solvation radius characterize the chemical effect of the solvent

#### **1. INTRODUCTION**

Water has long been known as a major component of magma, acting for instance as a flux promoting mantle melting in subduction zones or being the main driving force of magma buoyancy and volcanic eruptions. Water solution and dissolution reactions are thus of prime importance in igneous petrology. In this respect, a major difficulty faced when trying to understand the role of water is the extremely wide ranges of temperature, pressure and chemical composition, from ultramafic to silicic, to be dealt with from mantle conditions to surface. Furthermore, water contents as high as 7 wt % must be accounted for, which, given the low molar mass of water, makes water a major component of magma with contents of up to 20 mol %. Two other features complicate further the story. First, the H<sub>2</sub>O component dissolves in melts as both hydroxyl ions and molecular water<sup>1</sup> whose relative proportions vary with pressure, temperature and composition. Second, considerable experimental difficulties are met when investigating water in melts in situ. Actually, the fact that, after sample synthesis at high pressures, hydrous melts can be conveniently investigated at 1 bar above the glass transition has allowed much information to be gained on their physical properties (Richet et al., 1996). But such approaches remain to be complemented by much more extensive investigations.

In this respect, theoretical calculations are of great interest since they can in principle be performed readily for any condition of pressure, temperature and chemical compositions. As shown in a previous study of the  $SiO_2$ -H<sub>2</sub>O system up to 23 kbar and 2000°C (Ottonello et al., 2015), a major advantage of such calculations is that they do not necessarily require to consider the structure of the silicate framework because the truly

<sup>&</sup>lt;sup>1</sup> In the following we will in fact avoid the term "*water*" because it has a precise structural significance (i.e. liquid aggregation state). As we will amply recall in this text, the  $H_2O$  *component* actually dissolves in the silicate melt at molecular level, partly as un-reacted molecules [OH<sub>2</sub>] and partly as neutral hydroxyl functionals of polymer units [OH]°.

controlling parameters are the dielectric properties of the medium. In this new study we extend the work in Ottonello et al. (2015) based on Tomasi's Polarized Continuum Model (PCM; Floris and Tomasi, 1986; Floris et al., 1991; Tomasi and Persico, 1994; Tomasi et al., 1999) by treating the reactive solubility of a gaseous component in silicate melts of virtually any compositions. Here, we apply this computational procedure to the H<sub>2</sub>O component but stress that it could be extended to any gas-phase forming component exhibiting a reactive solubility (i.e. CO<sub>2</sub>, SO<sub>2</sub>, to quote only the two other most abundant volatile components) provided that sufficient experimental information is available to depict with the required accuracy the non-ideal contributions to the solute/solvent interaction. In the present paper we have taken advantage of the impressive amount of experimental observations of the H<sub>2</sub>O saturation surface in silicate melts of wide-ranging compositional and T,P regimes, carried out along half a century and gathered in the SOLWCAD database (Papale 1997, Papale et al., 2006), see Supplementary material.

#### **2. THEORY**

#### 2.1 Polarized Continuum Model (PCM) formulation of the Solvation Energy

Transferring a molecule from the isolated state of a gas phase to that of a solute within the melt involves various energy terms which, for the sake of simplicity, may be grouped to define a solvation energy contribution to the bulk Gibbs free energy of the substance. This Gibbs free energy of solvation ( $\Delta G^{\circ}_{solv}$ ) is made up of two main terms related to coupling work and molecular motion, which can themselves be further subdivided into several contributions (Tomasi and Persico, 1994):

$$\Delta G_{solv}^{0} = W(M/S) + \Delta G_{mm} = \Delta G_{el} + \Delta G_{cav} + \Delta G_{disp} + \Delta G_{rep} + RT \ln \left(\frac{q_{rot,g} \times q_{vib,g}}{q_{rot,s} \times q_{vib,s}}\right) - RT \ln \left(\frac{\rho_{M,g} \times \Lambda_{M,g}^{3}}{\rho_{M,s} \times \Lambda_{M,s}^{3}}\right)$$
(1)

where  $q_{rot,g}$ ,  $q_{vib,g}$ ,  $q_{rot,s}$  and  $q_{vib,s}$  are the microscopic contributions to the rotational and vibrational partition function in the gaseous state (subscript g) and in the solvent (subscript s), respectively,  $\rho_{M,g}$  and  $\rho_{M,s}$  are the number densities of the molecule M in the gas and in the solvent, and  $\Lambda_{M,g}$  and  $\Lambda_{M,s}$  are the momentum partition functions of M in the two states. The "*coupling work*" terms are the first four terms on the righthand side of Eq. 1. They include electrostatic solute-solvent interaction, cavitation, dispersion and repulsive contributions which are related to the work necessary to transfer the molecule M into the solvent (Tomasi

and Persico, 1994; Tomasi et al., 1999). For the solute molecule, interactions with the solvent perturbs its energy. This is quantum-mechanically expressed as:

$$[\hat{H}^0 + \hat{V}_R]\Psi = E\Psi$$
(2)

where  $\hat{H}^0$  is the Hamiltonian of the solute *in-vacuo*,  $\hat{V}_R$  the electrical potential of the reaction field, E is the energy and  $\Psi$  the solute wave function in solution. In the classical approximation (Floris and Tomasi, 1986; Floris et al., 1991) the sum of solute-solvent dispersive and repulsive interactions  $\Delta G_{disp} + \Delta G_{rep}$  is computed as double summations of terms extending to the solute atoms placed within the cavity and solvent atoms outside a cavity limited by a tessellated surface:

$$\Delta G_{dis} + \Delta G_{rep} = \sum_{a}^{s \text{ ol us } \alpha l \text{ ventt esserae}} \rho_s \sum_{i}^{s a_i \Gamma_{as}} A_i \Gamma_{as}$$
(3)

where  $\rho_s$  is the number density of the solvent in atomic units ( $\rho_s = N_s/V_s$ ) (i.e. number of solvent molecules N<sub>s</sub> per solvent volume V<sub>s</sub> expressed in Å<sup>-3</sup>), a<sub>i</sub> the area of the i<sup>th</sup> tessera composing the surface and  $\Gamma_{as}$  a set of dispersive and repulsive parameters obtained from crystallographic data (Caillet and Claverie, 1978). In a more recent implementation of PCM (Amovilli and Mennucci, 1997) the dispersive and repulsive contributions are expressed in terms of perturbing operators ( $\hat{h}_{rep}$ , $\hat{h}_{dis}$ . $\hat{X}_{dis}$ ) that act on the Atomic Orbital (AO) basis set:

$$\Delta \mathbf{G}_{\mathrm{rep}} = \left\langle \boldsymbol{\Psi} \middle| \hat{\mathbf{h}}_{\mathrm{rep}} \middle| \boldsymbol{\Psi} \right\rangle, \qquad (4)$$

$$\Delta \mathbf{G}_{\mathrm{dis}} = \left\langle \Psi \middle| \hat{\mathbf{h}}_{\mathrm{dis}} + \frac{1}{2} \hat{\mathbf{X}}_{\mathrm{dis}} \middle| \Psi \right\rangle.$$
 (5)

We remand to Amovilli and Mennucci (1997) for a detailed account of their nature and formal representation.

Practically, however, the operators are calibrated in such a way as to reproduce the effects obtained with the former procedure. Details on the tessellation procedures operated on molecular water  $[OH_2]$  are given in Supplementary material.

#### 2.2 Scaling Particle Theory (SPT) and the Cavitation Energy

The adopted formulation of Pierotti (1963,1965,1976) for the Gibbs free energy of cavitation ( $\Delta G_{cav}$ ) and its enthalpic and entropic components (H<sub>cav</sub>, S<sub>cav</sub>, respectively) is based on the scaled particle theory (SPT) of Reiss and coworkers (Reiss, 1965; Reiss et al., 1959, 1960, 1961). Denoting by  $\sigma_s$  the diameter of the solvent we express the reversible work necessary to create in the solvent a cavity of radius  $r \leq \sigma_s/2$  as:

$$\mathbf{W}_{0}(\mathbf{r},\boldsymbol{\rho}) = \mathbf{k} \operatorname{TI} \mathbf{n} \mathbf{p}_{0,\mathrm{i}}, \qquad (6$$

where k is Boltzmann constant and  $p_{0,i}$  the complement to 1 of the probability of finding a solute molecule i at the place of a solvent molecular center:

$$\mathbf{p}_{0,i} = \left(1 - \mathbf{p}_{0,r}\right) = \left(1 - \frac{4}{3}\pi r^{3}\rho_{s}\right). \tag{7}$$

To make room in the solvent for a solute of diameter  $\sigma_i$  the necessary cavity must have a radius  $r = \frac{\sigma_s + \sigma_i}{2}$ . Details on the PCM procedures adopted to reproduce the relative arrangements of solute and solvent molecules are given in Supplementary material (see also Ottonello et al., 2015).

Denoting by  $Y = \frac{\pi \rho_s \sigma_s^3}{6}$  the reduced number density and  $\zeta = \sigma_i / \sigma_s$ , we write the work done at atomic scale

as:

$$\frac{W(\mathbf{r},\rho)}{kT} = -\ln(1-Y) + \left(\frac{3Y}{1-Y}\right)\varsigma + \left[\left(\frac{3Y}{1-Y}\right) + \frac{9}{2}\left(\frac{Y}{1-Y}\right)^2\right]\varsigma^2 + \frac{YP}{\rho_s kT}\varsigma^3$$
(8)

where P is the (isotropic) pressure. The partial molar Gibbs free Energy of cavitation may be assumed to be equal to the reversible work  $\overline{G}_{cav} = W(\mathbf{r}, \rho) \equiv \Delta G_{cav}$ . The cavitation enthalpy at molar scale has the following form (Pierotti, 1976):

$$H_{c a v} = Y \alpha_{v} R \Gamma^{2} (1 - Y)^{-3} \left[ (1 - Y)^{2} + 3(1 - Y)\varsigma + 3(1 + 2Y)\varsigma^{2} \right] + \frac{N_{0}P}{\rho} \varsigma^{3}$$
(9)

where  $\alpha_V$  is the volume thermal expansion of the solvent and  $N_0$  is Avogadro's number, whereas the cavitation entropy may be obtained from the thermodynamic relationship (Pierotti, 1976)  $S_{cav} = -(\Delta G_{cav} - H_{cav})/T$ .

#### 2.3 Saturation surface of molecular water OH<sub>2</sub>

The partitioning of molecular water between a gas phase and a silicate liquid solvent can be assessed by (Ottonello et al., 2015):

$$\ln\left(\frac{f_{H_{2O}}}{x_{OH_{2,s}}}\right) = \frac{\overline{G}_{cav}}{RT} + \frac{\overline{G}_{int}}{RT} + \ln\left[\frac{RT}{x_{OH_{2,s}}\overline{V}_{OH_{2,s}} + (1 - x_{OH_{2,s}})\overline{V}_{s}}\right]$$
(10)

where  $f_{H2O}$  is the fugacity of H<sub>2</sub>O in the gas phase,  $\overline{G}_{int}$  is the summation of electrostatic dispersive and repulsive interactions and  $x_{OH2,s}$  is the molar fraction of H<sub>2</sub>O in the silicate liquid solvent. When the H<sub>2</sub>O component is sufficiently diluted, the molar volume of the solution is almost equal to the molar volume of the solvent  $\overline{V}_s$  and the right-hand side term reduces to the Henry's law constant for [OH<sub>2</sub>] in solution,  $\ln\left(\frac{f_i}{x_i}\right) = \ln K_{H,i}$ . Equation (10) is more generally valid as it applies to any concentration of [OH<sub>2</sub>] in solution, and, purposely, it does not contain any (model-dependent) configurational contribution arising from mixing in solution terms.

#### 2.4 Reactive solubility

There is a general consensus that the reactive solubility of  $H_2O$  in silicate melts is well represented by a homogeneous equilibrium among quasi-species of type (Silver and Stolper, 1985):

$$[OH_2]_{melt} + [O]_{melt}^0 \Leftrightarrow 2[OH]_{melt}^0$$
(11)

with the quasi-species mixing ideally on an hypothetical sub-lattice where the fractional molar amount of

H<sub>2</sub>O per unit mole of melt is  $x_{H_2O,sln} = x_{OH_2,sln} + \frac{x_{OH,sln}}{2}$  and the fractional molar amount of oxygen not associated to protons in any form is  $x_{O^0,sln} = 1 - x_{OH_2,sln} - x_{OH,sln}$ . Conversely, this simple conceptual scheme may be adopted to determine the relevant equilibrium constants from the experimentally observed bulk partitioning of the H<sub>2</sub>O component between the gaseous phase and liquid. It is sufficient for this purpose to express the fractional amount of hydroxyl terminations as the positive eigenvalue of a quadratic function in K<sub>11</sub> and x<sub>OH2,sln</sub> and to assume that scaling from the quasi-species lattice notation to molar fractions does not induce an excessive bias:

$$\mathbf{x}_{OH,sln}^{2} + \mathbf{K}_{11} \cdot \mathbf{x}_{OH_{2},sln} \cdot \mathbf{x}_{OH,sln} + \mathbf{K}_{11} \times \left(\mathbf{x}_{OH_{2,sln}}^{2} - \mathbf{x}_{OH_{2,sln}}\right) = 0$$
(12-1)

$$\mathbf{x}_{\mathrm{H}_{2}\mathrm{O},\mathrm{s}\mathrm{ln}} = \mathbf{x}_{\mathrm{OH}_{2},\mathrm{s}\mathrm{ln}} + \frac{\mathbf{x}_{\mathrm{OH},\mathrm{s}\mathrm{ln}}}{2}$$

$$K_{X,11} = \frac{X_{OH}^2}{X_{OH_2} \cdot X_O} = \prod X_{11}$$
(12-3)

(12-2)

#### 2.5 Hydrogen Bonding (HB) effects

The stabilizing effect originating in Hydrogen Bonding (HB) terms observed at low H<sub>2</sub>O contents in the H<sub>2</sub>O-SiO<sub>2</sub> mixed solvent by Ottonello et al. (2015) is not easily recast in terms of the current *ab-initio* formulation of the dispersion. HB takes place whenever discrete OH<sub>2</sub> molecules places themselves at the appropriate distance of OH-terminated polymers. Obviously, this sort of medium-range disorder prevents protons belonging to  $[OH_2]$  (see later) from being delocalized and stabilizes to some extent the molecular water with respect to neutral hydroxyl functionals  $[OH]^\circ$ . Detailed *ab initio* computations adopting the SSB-D Functional as implemented in NEWCHEM (Valiev et al., 2010) were carried out by Ottonello et al. (2015) on the  $[Si_5O_6(OH)_8]^\circ$  cluster (Figure 1). This is a good proxy of the fully polymerized tridimensional network in the presence of H<sub>2</sub>O in the system (a structure of intermediate Lewis acidity corresponding to the OH terminated analogue of the structure 4 of Civalleri et al., 1998; with three 4-membered rings). This structure,

which most likely forms in the  $SiO_2$ -rich portion of a  $H_2O$ - $SiO_2$  binary system, has 8 hydroxyl terminations, 2 of them pertaining to the two singly hydroxylated monomers.



**Figure 1**: HB effects in a polymerized melt. The net gain in stabilization at the athermal limit is  $E_{HB} \cong -44.5$  kJ/mol when molecular water [OH<sub>2</sub>] approaches a hydroxyl functional [OH]° of a singly-hydroxylated monomeric group, while it reduces to  $E_{HB} \cong -33.7$  kJ/mol for a doubly-hydroxylated monomeric group.

In the intermediate to low-acidity range the system is most likely completely depolymerized so that orthosilicic acid units  $[H_4SiO_4]^0$  are present. The SSB-D calculations (Ottonello et al., 2015) returned zeropoint  $\Delta H_{HB}$  energies of -44.5 kJ/mol when one OH<sub>2</sub> molecule approaches the OH functional of the singly hydroxylated monomer and of -33.7 kJ/mol when it approaches the OH functional of the doubly hydroxilated monomer. The  $\Delta H_{HB}$  energy is -39 kJ/mol when OH<sub>2</sub> approaches the orthosilicic acid unit (see Table 3 in Ottonello et al., 2015). Although they are consistent with the estimates of the  $\Delta H_{HB}$  energy in BLYP-D geometrically optimized structures of water (from -20.6 kJ/mol to -42 kJ/mol; Wendker et al.,2010) these energies do not correspond to the observations made along a simple H<sub>2</sub>O-SiO<sub>2</sub> binary system when moving from nominally anhydrous conditions to pure water. In fact, assuming K<sub>x,11</sub> = 0.11 (Silver and Stolper, 1985) and computing the electrostatic energy difference with a refined electrostatic scaling factor ( $\gamma_{el} = 1.0945$ )

differing from the nominal one ( $\gamma_{d} = 1.200$ ), Ottonello et al. (2015) obtained, for low H<sub>2</sub>O content, enthalpy differences consistent with the formation of an additional HB with respect to the hydrogen bonding state of H<sub>2</sub>O in pure water (i.e.  $\Delta H = -39$  kJ/mol at X<sub>H2O</sub>  $\cong$  0.06 at the athermal limit). However, moving in the two compositional directions, the HB contribution to the bulk solvation energy was still evident, but much less marked. It was thus obvious that the HB energy depends in a complex way on both the amounts of [OH]<sup>0</sup> functionals per monomeric group [H<sub>n</sub>SiO<sub>4</sub>]<sup>(4-n)-</sup> and the orientation of the polymeric clusters in the liquid. The electrostatic terms arising from HB may be treated classically through a fine tuning of the electrostatic radius (Ottonello et al., 2015). However, the large negative entropic terms associated with bond formation (and essentially due to substantial changes in the numbers and frequencies of the vibrational normal modes) progressively weakens the bond at increasing temperatures (cf. Table 3 in Ottonello et al., 2015). We will show here that one can arrive at a substantially correct appreciation of the role of HB in altering the homogeneous speciation by exploiting the SOLWCAD database (Supplementary Material). This is achieved through an inverse two-step non-linear approach first returning provisional  $\Delta H^{\circ}_{HB}$ ,  $\Delta S^{\circ}_{HB}$ ,  $\Delta V^{\circ}_{HB}$  energy terms (assumed invariant with T and P) and then fine tuning 2<sup>nd</sup> order interaction in terms of regular Redlich-Kister contributions expanded in terms of bulk molar amount of H<sub>2</sub>O in solution (RK<sub>H</sub>, RK<sub>S</sub>, RK<sub>V</sub>)

#### **3.** CALCULATIONS

The first step is the parameterization of the solvent in the framework of the Integral Equation Formalism of the Polarized Continuum Model (IEFPCM). As summarized here, this was done a few years ago from the observed solubility of non-reacting species (Ar and other rare gases) in silicate melts of various composition (Ottonello and Richet, 2014). The electrostatic interactions between the "*nominally*" inert elements He, Ne, Ar, Kr, Xe, Rn and the medium in which they are dissolved are virtually negligible, but an accurate description of polarizabilities and permanent moments is crucial to depict the weak interactions taking place. Nevertheless, the most important parameter to be assessed is the "*solvation radius*" r<sub>s</sub> of a silicate melt of variable composition (and the ensuing solvation diameter  $\sigma_s = 2 \times r_s$ ). Although the assumption of a spherical shape for the solvent molecules has the obvious advantage of eliminating solvent orientation around the solute, this assumption ( $\sigma_s = \sqrt[3]{6V/\pi}$ ) results in a large overestimation of the appropriate value assigned to

the real solvent. The  $\sigma_s$  appropriate to silicate melts was retrieved through an inverse modeling application of SPT, and fits nicely the trend between a non polar (C<sub>6</sub>H<sub>6</sub>) and a polar solvent (H<sub>2</sub>O) (see Figure 6 in Ottonello and Richet, 2014). It is satisfactorily reproduced by a simple expression in the form  $\sigma_s = 2 \times (1.1383r_{coll} - 0.3836)$  where  $r_{coll}$  is the Stearn -Eyring collisional radius (i.e.  $r_{coll} = \sqrt[3]{V/8}$ ) and the molecular volume V is based on molar volumes calculated with the procedure of Bottinga et al. (1983) and scaled to the atomic level.

Other parameters to be assessed are the static dielectric constant of the medium  $\varepsilon$  and the dielectric constant at infinite frequency  $\varepsilon^{\infty}$ . Provisional values of the static dielectric constant  $\varepsilon$  were derived from a modified form of the Clausius-Mossotti relation:

$$\frac{\varepsilon - 1}{\varepsilon + 2} \cong \frac{4\pi}{3V_s} \sum_{j}^{\text{oxi des}} x_j \alpha_j^{\text{st ati}}$$
(13)

where  $\alpha_i^{\text{static}}$  is the static polarizability. Moreover, at optical frequencies, we posited

$$\frac{\varepsilon^{\infty}-1}{\varepsilon^{\infty}+2} = \frac{n^2-1}{n^2+2},\qquad(14)$$

where the refractive index n varies within a restricted range (Vo-Thanh et al., 2005), namely, 1.58 to 1.64.

The non marginal role of the dielectric constant in the solute/solvent interaction may be fully appreciated when recalling that the electrical potential of the reaction field  $V_R$  (eq. 2) obeys, within the solvent, the linearized Poisson-Boltzmann equation

$$-\varepsilon \nabla^2 \mathbf{V}_{\mathbf{R}} + \varepsilon \mathbf{k}^2 \mathbf{V}_{\mathbf{R}} = 0, \qquad (15)$$

where  $\kappa$  (the inverse of the Debye length) is

$$\kappa = \frac{8\pi IF}{\varepsilon RT}, \qquad (16)$$

with I = ionic strength of the solvent and F = Faraday constant (see Vetuschi Zuccolini et al., 2011; for a practical application of the equations 15-16 to aqueous solutions).

Whereas the partial molar Gibbs free energy required to create a cavity in a fluid of hard spheres  $\overline{G}_{cav}$  is based on the statistical mechanical theory of fluids and the properties of exact radial distribution functions (Reiss,

1965; Reiss et al., 1959, 1960, 1961), the interaction energy  $\overline{G}_{int} = \Delta G_{elec} + \Delta G_{disp} + \Delta G_{rep}$  is obtained *ab initio* from the IEFPCM<sup>2</sup>. In Figure 2 are drawn the electrostatic (E<sub>elec</sub>), inductive (E<sub>disp</sub>) and repulsive(E<sub>rep</sub>) energy terms computed with the GAUSSIAN package (Frisch et al., 2004) for a series of silicate melts aiming to cover the compositional range observed in nature. These are the same substances investigated in the past to parameterize the solvent properties (Ottonello and Richet, 2014). Pure silica was also investigated as a reference medium (see later).



**Figure 2**: Bulk solute/solvent interaction and its various components, resolved for a silicate melts population deemed to be sufficiently representative of the natural compositional realm (Ottonello and Richet, 2014) and plotted against the number density of the solvent. Open symbols denote calculations carried out with  $\gamma_{el}$ =1.0945 instead of the nominal value  $\gamma_{el}$ =1.20 (filled symbols). The resulting electrostatic interaction is enhanced of roughly -10.9 kJ/mol, stabilizing further the molecular water in the silicate liquid. The bulk interaction energy may be represented through a linear regression over the number density  $E_{int}/(kJ\times mol^{-1}) = -20.803 - 834.71\times (\rho/Å^3)$  with a sufficiently high correlation coefficient ( $R^2 = 0.8821$ ).

Calculations were carried out at the DFT/B3LYP theory level with a 6-31+G(d,p) basis set. The radii adopted to conform the Solvent Accessible Surface (SAS) of Tomasi's model are the UAHF (United Atom

 $<sup>^{2}</sup>$  Because the three forms of energy are purely enthalpic in nature the identification with the corresponding Gibbs free energy is immediate.

Topological Model applied on radii optimized for the HF/6-31G(d) theory level). The adopted electrostatic scaling parameter ( $\gamma_{el}$ =1.0945 instead of the nominal values  $\gamma_{el}$  = 1.2) reproduces satisfactorily the partial molar volume of [OH<sub>2</sub>] in pure silica liquid (V<sub>OH2</sub> ~ 12 cm<sup>3</sup>/mol) through an appropriate account of the volume of interaction in a nominally anhydrous melt.

When plotted against the number density of the solvent ( $\rho$ ) the discrete values of the various forms of energy exhibit regular trends, which may be replaced by continuous first-order functions (Figure 2). Particularly, the bulk interaction is described with sufficient precision ( $R^2 = 0.882$ ) with the approximation  $E_{int}/(kJ \times mol^{-1}) = -20.803 - 834.71 \times (\rho/Å^3)$ . The adoption of a continuous function for replacing discrete *ab-initio* calculations is not compulsory, but allows a significant reduction of computational time when operating on an extended database (see later).

One may obtain the gas phase fugacity of  $H_2O$  ( $f_{H2O}$  in eq. 10) by adopting the Kerrick and Jacobs modification of the Redlich-Kwong equation of state (EOS) at all P,T of interest (Kerrick and Jacobs, 1981; Jacobs and Kerrick, 1981), or other equations of state (i.e. the SUPERFLUID algorithm of Belonoshko et al., 1992; and/or the formalism of Pitzer and Sterner, 1994). Uncertainties associated with the various EOS are virtually inconsequential in the error propagation associated with the numerical resolution of the inverse problem (see Supplementary material).

#### 3.1 A simple test case: the AOQ anhydrous rhyolite ( $Qz_{38}Ab_{38}Or_{34}$ )

There are at present good experimental data concerning the homogeneous speciation of water, essentially based on infrared and Raman spectroscopy studies on quenched materials, showing that the observed partitioning of the H<sub>2</sub>O component into  $[OH_2]$  and  $[OH]^0$  may be approximately recast in terms of quasi-species ideally mixing into an appropriate sub-lattice. In an extensive review of speciation, solubility and diffusion of the H<sub>2</sub>O component in rhyolitic glasses and melts, Zhang (1999) focused on the AOQ Rhyolite (SiO<sub>2</sub> = 76.14 wt%; Al<sub>2</sub>O<sub>3</sub> = 13.53; Na<sub>2</sub>O = 4.65; K<sub>2</sub>O = 5.68; corresponding to the normative composition Qz<sub>38</sub>Ab<sub>38</sub>Or<sub>34</sub>). For this substance there is detailed information concerning the amount of bulk dissolved H<sub>2</sub>O at various P,T conditions and its speciation (Holtz et al., 1992, 1995; Nowak and Behrens, 1995; 2001). The fictive molar volume of the nominally anhydrous AOQ melt at room conditions, according to the procedure

of Bottinga et al. (1983), is 27.795 cm<sup>3</sup>/mol, corresponding to a number density of ~ 0.0217 Å<sup>-3</sup> and the thermal expansion coefficients are  $\alpha_0 = 2.51$ E-5 K<sup>-1</sup>,  $\alpha_1$ =-0.618E-9 K<sup>-2</sup>. The isothermal compressibility is calculated according to the procedure of Rivers and Charmichaels (1987) as 6.824 Mbar<sup>-1</sup>. The static polarizability is  $\alpha^{\text{static}} = 5.462$  Å<sup>3</sup>, the relative static dielectric constant is  $\varepsilon = 3.949$  and the dielectric constant at infinite frequency is  $\varepsilon^{\infty} = 2.600$ . The solvation radius is 1.658 Å. We must now briefly recall the relationships among the various quantities intervening in the solution process. The bulk Gibbs free energy of solution for a gaseous, monoatomic species in its stable standard state is simply related to the Henry's Law constant K<sub>H</sub> by:

$$\Delta G_{\rm S} = \mathbf{R} \Gamma \ln \mathbf{K}_{\rm H} = \Delta \overline{\mathbf{G}}_{\rm c \ a \ v} + \Delta \overline{\mathbf{G}}_{\rm e \ l} + \Delta \overline{\mathbf{G}}_{\rm d \ i \ s \ p} + \Delta \overline{\mathbf{G}}_{\rm r \ e \ p} + \mathbf{R} \Gamma \ln \left( \frac{\mathbf{R} \Gamma}{\overline{\mathbf{V}}_{\rm s}} \right)$$
(17)

where  $\overline{V}_s$  is the molar volume of the solvent. Adoption of this simplified form implies that one assumes the rotational, vibrational and momentum partition functions to be identical in the two states, i.e. isolated molecule and solute molecule (cf. Eq. 1).

The enthalpy of solution is given by the following partial derivative of Henrys'Law constant (Pierotti, 1976):

$$\Delta \mathbf{H}_{\mathrm{S}} = \left(\frac{\partial \ln \mathbf{K}_{\mathrm{H}}}{\partial (1/\mathrm{R}\Gamma)}\right)_{\mathrm{P}} = \overline{\mathbf{H}}_{\mathrm{cav}} + \overline{\mathbf{H}}_{\mathrm{e}1} + \overline{\mathbf{H}}_{\mathrm{d}\,\mathrm{i}\,\mathrm{s}\,\mathrm{p}} + \overline{\mathbf{H}}_{\mathrm{r}\,\mathrm{e}\,\mathrm{p}} + \alpha_{\mathrm{s}}\mathrm{R}\Gamma^{2} \qquad (18)$$

where  $\alpha_s$  is the thermal expansion coefficient of the solvent. The entropy of solution is (Pierotti, 1976):

$$\Delta \mathbf{S}_{\mathrm{S}} = -\left(\frac{\partial \Delta \mathbf{G}_{\mathrm{s}}}{\partial \Gamma}\right)_{\mathrm{P}} = \overline{\mathbf{S}}_{\mathrm{c}\,\mathrm{a}\,\mathrm{v}} + \overline{\mathbf{S}}_{\mathrm{e}\,\mathrm{l}} + \overline{\mathbf{S}}_{\mathrm{d}\,\mathrm{i}\,\mathrm{s}\,\mathrm{p}} + \overline{\mathbf{S}}_{\mathrm{r}\,\mathrm{e}\,\mathrm{p}} - \mathbf{R} \mathbf{1} \mathbf{n} \left(\frac{\mathbf{R}\Gamma}{\overline{\mathbf{V}}_{\mathrm{s}}}\right) + \alpha_{\mathrm{s}} \mathbf{R} \Gamma \quad (19)$$

The isobaric heat capacity of solution is (Pierotti, 1963;1965):

$$\Delta C_{P_s} = \overline{C}_{P_{c a}} + \overline{C}_{P_{e l}} + \overline{C}_{P_{d i s}} + \overline{C}_{P_{r e p}} + 2\alpha_s R\Gamma + R\Gamma^2 (\partial \alpha_s / \partial \Gamma)_p$$
(20)

with

$$\overline{C}_{P_{c a v}} = \left[\frac{2}{T} - \alpha_{s} + \frac{(\partial \alpha_{s}/\partial \Gamma)_{p}}{\alpha_{s}}\right] \times \overline{H}_{c a v} - R\left[\frac{Y\alpha_{s}T}{(1-Y)^{2}}\right]^{2} \times \left[(1-Y)^{2} + 6\varsigma(1-Y) + 3\varsigma^{2}(4Y+5)\right]$$
(21)

where  $\overline{H}_{cav}$  is given by Eq. 9 without the last term on the right-side and

$$\overline{C}_{Pel} + \overline{C}_{Pdis} + \overline{C}_{Prep} \overline{C}_{Prep} = \alpha_s \times \left(\overline{H}_{el} + \overline{H}_{dis} + \overline{H}_{rep}\right)$$
(22)

To address properly all these energy terms we must introduce some simplifying assumptions, namely, that the electronic, dispersive and repulsive contributions to the Gibbs free energy of solution in Eq. 17 are purely enthalpic (which is implicit in the *ab-initio* assessment). With this proviso, the corresponding entropic terms in Eq. 19 vanish.

For the nominally anhydrous melt at 25°C and P = 1bar we obtain  $G_{CAV} = 17.726$  kJ/mol;  $H_{INT} = -38.888$  kJ/mol;  $H_{CAV} = 0.294$  kJ/mol;  $S_{CAV} = -58.467$  J/(mol×K);  $G_S = -4.321$  kJ/mol;  $H_S = -41.054$  kJ/mol;  $S_S = -123.202$  J/(mol×K). At room conditions the (adimensional) Henry's Law constant is simply the reciprocal of the solubility constant, i.e.  $lnK_S = 1.743$ ;  $LnK_H = -1.743$ .

Let us now assume that  $H_2O$  and AOQ mix without appreciable excess contributions. Computing the values of  $K_{11}$  appropriate to reproduce the observed bulk amount of  $H_2O$  in solution at the various P,T conditions (X  $H_2O_{(obsv)}$  in Table 1) and arranging them in an Arrhenius plot (Figure 3), we see that the observed biases in the various EOS induce negligible error propagation although ideality breaks. In fact, the computed  $K_{11}$  is systematically higher than the values predicted by the regression of Nowak and Behrens (1995), which is essentially based on in-situ IR observations.



**Figure 3**: nominal values of  $K_{11}$  computed with the SPT-PCM approach with different EOS for the gaseous phase, compared with the regression of Nowak and Behrens (1995) which is based on in-situ IR observations.

The sub-parallel downward shift of the nominal  $\ln K_{11} = f(T^{-1})$  in Figure 6 implies that excess terms in solution are present. As anticipated, these terms are due to medium-range ordering promoted by HB that

prevents the  $[OH_2]$  molecules from assuming a correct orientation with respect to the  $[O^-]$  functionals in order to delocalize partially the protons and create neutral hydroxyl terminations  $[OH]^\circ$ . It has been also anticipated that one easily retrieves these energy terms by treating the system as non-isometric in terms of a simple one-parameter regular (i.e. symmetric in the compositional realm of the system) Redlich-Kister expansion on the amount of  $OH_2$  in solution.

Taking into account the HB perturbation, we reproduce sufficiently well the observed amount of bulk  $H_2O$  in solution (Figure 4). Calculation details are listed in Table 1.



**Figure 4**: SPT-PCM calculations for the AOQ granitic composition compared to the experimental observations of Holtz et al. (1992, 1995) The HB contributions are included as an additional term of the electrostatic interaction  $G_{HB}(eV) = \Delta H^{\circ}_{HB} - T \times \Delta S^{\circ}_{HB} + P \times \Delta V^{\circ}_{HB} + G_{HB,excess} = 1.831 \times 10^{-1} \cdot 2.114 \times 10^{-7} \times T(K) + 6.329 \times 10^{-9} * P(bar) + X_{H2O} \times (1 - X_{H2O}) \times [-5.480 \times 10^{-2} - 2.635 \times 10^{-7} \times T(K) - 2.923 \times 10^{-8} \times P(bar)]$  with the first three terms resolved through inverse methods operating on an extended database (i.e. 970 samples) and the excess contributions obtained with a fine tuning based on the observations of (Holtz et al., 1992, 1995).

**Table 1**: SPT-PCM calculations for the AOQ Rhyolite. The bulk  $H_2O$  amount in solution after Holtz et al. (1992, 1995) is compared with the model results on a 1 O pfu basis. The amount of  $[OH_2]$  in the liquid is first computed with the SPT-PCM procedure. Stabilizing HB effects are then added to the interaction energy and the calculation is brought to completion. The homogeneous speciation in solution, and the ensuing amount of [OH] functionals is based on the homogeneous speciation constant after Nowak and Behrens (1995). The fugacity is computed with the Kerrich-Jacobs EOS. See text for the significance of the remaining parameters.

Sample	Т (К)	P (Gpa)	f (GPa)	G <sub>CAV</sub> (kJ/mol)	G <sub>INT</sub> (kJ/mol)	G <sub>HB</sub> (kJ/mol)	G <sub>HB,excs</sub> (kJ/mol)	InK <sub>H</sub>	X <sub>H20 (obsv)</sub>	X <sub>H2O</sub> (calc)	Х <sub>[ОН2]</sub>	X <sub>[OH]</sub>
Z1	973	0.50	0.384	64.360	-45.950	0.884	-6.535	10.382	0.154	0.157	0.071	0.174
Z2	1023	0.20	0.148	63.585	-45.697	-1.977	-3.908	10.11	0.098	0.097	0.031	0.134

Z3	1073	0.03	0.029	64.320	-44.926	-4.041	-1.613	10.429	0.037	0.037	0.005	0.064
Z4	1073	0.05	0.046	64.604	-45.360	-3.918	-2.062	10.357	0.048	0.049	0.009	0.081
Z5	1073	0.05	0.046	64.604	-45.360	-3.918	-2.062	10.367	0.047	0.049	0.009	0.081
Z6	1073	0.05	0.046	64.604	-45.360	-3.918	-2.062	10.339	0.05	0.049	0.009	0.081
Z7	1073	0.07	0.063	64.877	-45.672	-3.795	-2.414	10.262	0.064	0.058	0.012	0.093
Z8	1073	0.07	0.063	64.877	-45.672	-3.795	-2.414	10.264	0.063	0.058	0.012	0.093
Z9	1073	0.10	0.086	65.276	-46.015	-3.611	-2.844	10.268	0.069	0.070	0.016	0.108
Z10	1073	0.10	0.086	65.276	-46.015	-3.611	-2.844	10.273	0.069	0.070	0.016	0.108
Z11	1073	0.10	0.086	65.276	-46.015	-3.611	-2.844	10.269	0.069	0.070	0.016	0.108
Z12	1073	0.13	0.108	65.667	-46.269	-3.427	-3.205	10.234	0.083	0.079	0.020	0.119
Z13	1073	0.14	0.115	65.796	-46.341	-3.366	-3.315	10.238	0.085	0.082	0.021	0.123
Z14	1073	0.20	0.159	66.562	-46.691	-2.997	-3.916	10.281	0.096	0.097	0.028	0.139
Z15	1073	0.20	0.159	66.562	-46.691	-2.997	-3.916	10.283	0.096	0.097	0.028	0.139
Z16	1073	0.20	0.159	66.562	-46.691	-2.997	-3.916	10.286	0.095	0.097	0.028	0.139
Z17	1073	0.30	0.241	67.821	-47.130	-2.384	-4.811	10.372	0.119	0.118	0.038	0.160
Z18	1073	0.30	0.241	67.821	-47.130	-2.384	-4.811	10.372	0.119	0.118	0.038	0.160
Z19	1073	0.40	0.339	69.072	-47.513	-1.770	-5.672	10.51	0.139	0.138	0.049	0.178
Z20	1073	0.48	0.433	70.069	-47.813	-1.279	-6.361	10.628	0.145	0.153	0.058	0.190
Z21	1073	0.50	0.459	70.319	-47.888	-1.156	-6.534	10.667	0.152	0.157	0.060	0.193
Z22	1073	0.50	0.459	70.319	-47.888	-1.156	-6.534	10.672	0.154	0.157	0.060	0.193
Z23	1073	0.50	0.459	70.319	-47.888	-1.156	-6.534	10.666	0.151	0.157	0.060	0.193
Z24	1073	0.50	0.459	70.319	-47.888	-1.156	-6.534	10.67	0.154	0.157	0.060	0.193
Z25	1073	0.50	0.459	70.319	-47.888	-1.156	-6.534	10.671	0.154	0.157	0.060	0.193
Z26	1073	0.50	0.459	70.319	-47.888	-1.156	-6.534	10.668	0.152	0.157	0.060	0.193
Z27	1073	0.80	1.018	74.048	-49.092	0.686	-9.219	11.282	0.202	0.218	0.100	0.236
Z28	1073	0.80	1.018	74.048	-49.092	0.686	-9.219	11.266	0.199	0.218	0.100	0.236
Z29	1123	0.10	0.089	68.250	-46.997	-4.631	-2.835	10.45	0.068	0.069	0.014	0.110
Z30	1123	0.20	0.169	69.538	-47.692	-4.017	-3.927	10.441	0.094	0.097	0.025	0.144
Z31	1123	0.50	0.492	73.299	-48.885	-2.176	-6.552	10.813	0.159	0.156	0.055	0.201
Z32	1173	0.05	0.048	70.549	-47.335	-5.958	-2.039	10.728	0.047	0.048	0.007	0.082
Z33	1173	0.05	0.048	70.549	-47.335	-5.958	-2.039	10.77	0.043	0.048	0.007	0.082

Z34	1173	0.20	0.177	72.515	-48.697	-5.037	-3.941	10.579	0.095	0.097	0.023	0.148
Z35	1223	0.20	0.184	75.492	-49.707	-6.058	-3.956	10.732	0.090	0.096	0.021	0.151
Z36	1273	0.05	0.049	76.495	-49.340	-7.998	-2.036	11.127	0.040	0.047	0.005	0.083
Z37	1273	0.50	0.571	82.243	-51.931	-5.236	-6.636	11.154	0.162	0.154	0.044	0.220
Z38	1323	0.20	0.195	81.445	-51.737	-8.098	-3.991	10.964	0.092	0.095	0.017	0.155
Z39	1373	0.05	0.049	82.443	-51.362	-10.038	-2.045	11.371	0.042	0.046	0.004	0.084
Z40	1373	0.20	0.199	84.422	-52.755	-9.118	-4.010	11.095	0.088	0.094	0.016	0.157
Z41	1373	0.50	0.608	88.205	-53.984	-7.276	-6.704	11.356	0.165	0.152	0.037	0.228
Z42	1373	0.50	0.608	88.205	-53.984	-7.276	-6.704	11.344	0.162	0.152	0.037	0.228
Z43	1423	0.20	0.202	87.399	-53.776	-10.138	-4.029	11.182	0.090	0.093	0.014	0.158
Z44	1423	0.20	0.202	87.399	-53.776	-10.138	-4.029	11.193	0.088	0.093	0.014	0.158
Z45	1473	0.05	0.050	88.391	-53.396	-12.078	-2.060	11.642	0.040	0.045	0.003	0.084
Z46	1473	0.10	0.100	89.071	-54.047	-11.772	-2.874	11.436	0.060	0.065	0.007	0.117
Z47	1473	0.30	0.326	91.650	-55.293	-10.544	-5.017	11.269	0.116	0.114	0.019	0.189
Z48	1473	0.40	0.468	92.912	-55.691	-9.930	-5.910	11.352	0.136	0.132	0.026	0.213
Z49	1473	0.50	0.636	94.167	-56.044	-9.316	-6.772	11.519	0.164	0.149	0.032	0.234
Z50	1623	0.10	0.102	97.996	-57.113	-14.832	-2.915	11.758	0.058	0.064	0.005	0.117

We may immediately appreciate in Table 1 the dominant role of cavitation energy (essentially entropic in nature) partially counterbalanced by the electrostatic + inductive + repulsive interactions (apparently purely enthalpic, though with hidden volumetric effects, cf. eq. 9). The HB terms that stabilize the molecular form  $[OH_2]$  ( $G_{HB} + G_{HB,exc}$ ) are subordinate and reduce to a few kJ/mol when summed up together. It should be stressed that these terms may vary to some extent, depending on the value assigned to  $K_{X,11}$ , which is a model-dependent parameter essentially based on conditional constants<sup>3</sup>.

#### 3.2 The SOLWCAD dataset

In the previous example we adopted provisional estimates of  $K_{X,11}$  based on detailed spectroscopic investigations on a given silicate sample at different P,T conditions. We explore the possibility of detecting how the thermodynamic parameters of a compositionally invariant speciation constant may be retrieved from

<sup>&</sup>lt;sup>3</sup> In thermodynamics a conditional constant is an a-dimensional magnitude obtained when replacing thermodynamic activities with model-dependent molar fractions. The obtained constant is valid only at the P,T,X conditions of the investigation, i.e. "conditional".

the realm of observations hitherto available in terms of simple bulk solubility of the  $H_2O$  component at saturation, in the absence of any data concerning the homogeneous speciation in the liquid. To do this we benefit from the extensive data collection assembled in the past (Papale et al., 2006) to retrieve with an inverse procedure the thermodynamic parameters of the homogeneous speciation and interpret the results within the conceptual framework of the Polarized Continuum Model. We will apply this exercise both on the extended database of 970 samples (hereafter "*raw data*") set up by Papale et al. (2006) to parameterize their thermodynamic regular-non isometric mixing model with the SOLWCAD package (Papale, 1997) as well as on the SOLWCAD-refined database. Although the database dates to 2006, its stability and internal consistency is such that the SOLWCAD calibration carried out by Papale et al. (2006) produces model parameters that do not differ appreciably from those calibrated in 1997 with nearly 10 years of data less. That suggests that the database employed here, and the SOLWCAD calculations, provide a representative sample of bulk H<sub>2</sub>O solubility in silicate melts over a wide P-T-compositional spectrum of interest. The computed K<sub>11</sub> values that return the observed bulk fractional amount of the H<sub>2</sub>O component in solution (one O molar basis) are arranged in an Arrhenius plot in Figure 5.



**Figure 5**: Arrhenius plot of the computed  $K_{11}$  constants returning the observed bulk fractional amount of  $H_2O$  in solution (970 samples; 1 O pfu basis). Neglecting volume effects, the best interpolant is  $lnK_{11} = 5.6585-5117.1/T$ . Regression lines for the SOLWCAD refined population (Papale et al., 2006) and for the AOQ composition are reported for comparative purposes. The gap with the conditional constant after Nowak and Behrens (1995) may be eventually expressed in terms of a mean value of productorials of activity coefficients (i.e.  $lnK_{\gamma}$  in figure).

The regression on reciprocal absolute T allows us to retrieve the provisional enthalpy and entropy of reaction as  $\Delta H_{11} = 42.547$  (44.664) kJ/mol,  $\Delta S_{11} = 47.049$  (47.472) J/(mol×K), with values in brackets referred to the model-refined dataset. Application of the obtained parameters in a direct way returns the bulk amount of  $H_2O$  in solution, which, when compared to the experimental population proves to be reasonably accurate given the simplicity of the procedure. The mean error is in fact 3.57 kJ/mol in terms of energy and  $\sim 0.012$  in terms of bulk fractional molar amount of  $H_2O$  in the melt (1 O pfu) when operating on the raw data. With the SOLWCAD-refined dataset, the error of the ideal procedure remains practically the same (i.e. a mean error of  $\sim 3.65$  kJ/mol in terms of energy and  $\sim 0.011$  in terms of bulk fractional molar amount of H<sub>2</sub>O in the liquid, on a 1 O pfu basis). Adopting a non-linear minimization procedure and letting the volume of reaction be different from zero does not ameliorate the fits for both data populations. The most striking evidence arising from this sort of plot is however, the fact that the K<sub>11</sub> model regression operated on the raw data population (970 data) is nearly coincident with the one obtained on the peculiar AOQ "granitic" composition. Looking in detail at the result of the ideal model it turns out that both populations (raw data and SOLWCAD refined data) are slightly underestimated (i.e. regression slope ~0.931 for both populations; Figure 6) with two outliers at P= 3 GPa in the SOLWCAD refined population, which is overall less dispersed, confirming the internal efficiency of the SOLWCAD procedure for lower pressures.



**Figure 6**: Results of the SPT-PCM procedure applied to the 970 samples of the dataset assembled by Papale et al. (2006), applying  $lnK_{11} = 5.6585-5117.1/T$  (raw data) and  $lnK_{11} = 5.7094-5371.8/T$  (SOLWCAD refinement).

Arranging the biases with respect to the observed bulk fractional amount of  $H_2O$  component in solution (Figure 7) it is seen moreover that, if the interpolant regressions (i.e. the above anticipated provisional enthalpy and entropy of reaction for the two populations) is adopted, the observed dispersion (Figure 6) turns out to be a reasonably well behaved function of the observed bulk amount of the  $H_2O$  component in solution (Figure 7).



Figure 7: Ideal model biases at the various bulk fractional amounts of  $H_2O$  component in solution.

The observed biases may be substantially reduced when taking into account the stabilizing effects of the HB on the molecular form  $OH_2$  in solution. By employing again the regression of Nowak and Behrens (1995) for  $K_{X,11}$ , a non-linear minimization procedure carried out on the extended database returns the following HB energy terms  $\Delta H^{\circ}_{HB} = 1.831 \times 10^{-1} \text{ eV}$ ;  $\Delta S^{\circ}_{HB} = 2.114 \times 10^{-7} \text{ eV/K}$ ;  $\Delta V^{\circ}_{HB} = 6.329 \times 10^{-9} \text{ eV/bar}$ ;  $RK_H = -2.481 \times 10^{-1} \text{ eV}$ ;  $RK_s = 8.883 \times 10^{-8} \text{ eV/K}$ ;  $RK_v = -3.637 \times 10^{-9} \text{ eV/bar}$ . Although the excess volume contributions are limited, the non-isometric expansion  $G_{HB,excess} = X_{H2O} + (1-X_{H2O})^* [RK_H - T \times RK_S + (P-1) \times RK_V]$  is justified by the necessity of reducing the biases observed at high P and proves to be correct when analyzing the lack of internal correlation of T-dependent and P-dependent terms. The mean error in terms of energy on 970 samples is thus reduced to ~2.137 kJ/mol. In terms of computed bulk molar abundance of H<sub>2</sub>O in solution the mean error is 0.0172 moles per unit mole of melt (0.0094 when operating on a 1 O pfu basis). Applying the model to the SOLWCAD refined dataset, the biases are further reduced (i.e. a mean error of 0.0157 moles of H<sub>2</sub>O per unit mole of melt or 0.0086 moles of H<sub>2</sub>O when operating on a 1 O pfu basis). Both populations are well distributed, with correlations not far from the identity line (Figure 8) and a Gaussian shaped dispersion. Detailed calculations are listed in Table S.1 of the Supplementary material.



**Figure 8**: Ab-initio vs SOLWCAD-refined and raw data populations (970 samples in each set). The simple regression for the sub-regular model is in both cases not far from the identity line, with a more marked dispersion when operating on the SOLWCAD-refined set, essentially due to the two outliers at P = 3 GPa. The inset shows the frequency distribution of the normalized error [difference between calculated and observed (or refined) value normalized to the observed (or refined) one] for the two polulations.

#### 4. DISCUSSION

#### 4.1 The energy of quasi-species end the role of dielectric continuum

As outlined by Moretti et al. (2014), to describe completely the dissolution of  $H_2O$  in melts a reaction space of dimension 4 is required (i.e. 7 species and 3 independent conservation equations; see also Thompson, 1969; and Kress, 2003). For the sake of simplicity we drop here the free hydroxyls  $[OH]^-$  deriving from autoprotolytic reaction of the  $[OH_2]$  molecule, whose amount in solution is still the object of controversy, and describe the interaction of molecular water with a formally anhydrous melt as composed of 3 distinct processes: a full ionic dissociation of molecular water (11-1), inducing de-polymerization of the silica network (11-2), followed by neutralization of the polymer functional by free protons (11-3):

$$OH_{2,sln} \Leftrightarrow 2H_{sln}^+ + O_{sln}^{2-}$$
 (11-1)

$$O_{sln}^{2-} + O_{sln}^{0} \Leftrightarrow 2O_{sln}^{-}$$
(11-2)  
$$2O_{sln}^{-} + 2H_{sln}^{+} \Leftrightarrow 2OH_{sln}^{0}$$
(11-3)

This line of thinking proves correct when detailed first principles computations are carried out (see later), but could at first sight be misleading. Indeed, for simple electrostatic reasons,  $[OH_2]$  molecules position themselves preferably between two polymeric terminations, as schematically shown in Figure 9.



**Figure 9**: Effects of partial delocalization of H centers about the oxygen of  $[OH_2]$ : from an initial condition of complete localization, where 3 normal vibrational modes are present (blue circle) hydrogens become progressively localized on the O- centers of neighbouring polimeric units (red circles). The OH stretching motions becomes then progressively more intense.

The two protons nominally pertaining to  $[OH_2]$  become partly delocalized from the central oxygen of  $[OH_2]$ and partly localized on the two O<sup>-</sup> belonging to the two neighboring polymer (or monomer) units: this (and nothing else) is the information yielded by the IR spectra. In plain terms, what one basically sees is

$$OH_{2,sln} + 2O_{sln}^{-} \Leftrightarrow 2OH_{sln}^{0} + O_{sln}^{2-}$$
(11-4)

The reaction actually is completely displaced leftward and could not proceed without the concomitant depolymerization reaction step 11-2.

It is obvious that the process, besides the anticipated HB medium range effects, is not influenced appreciably by the composition (and long-range structure) of the melt but simply by its polarization properties.

We may prove this statements by analyzing conveniently the energy properties of the reacting quasi-species in the framework of the IEFPCM model, identifying them with the corresponding species in their appropriate

multiplicity state. As examples, we did calculations in this manner, assuming the various moieties to be immersed in a dielectric continuum having the properties of pure molten silica (Table 2).

Table 2: B3LYP/IEFPCM energy of selected moieties in a solvent with the dielectric properties of molten silica (dielectric constant  $\epsilon = 3.525$ ; dielectric constant at infinite frequency  $\epsilon_{\infty}=2.6$ ; statistical solvent diameter  $\sigma_S = 3.262$  Å; numeral density  $\rho = 0.02254$  Å<sup>-3</sup>; thermal expansion  $\alpha = -1.0 \times 10^{-6}$  K<sup>-1</sup>). The adopted basis set is 6-31G+(d,p). E<sub>SS</sub> = electrostatic solute-solvent interaction; E<sub>DISP</sub> = dispersive energy; E<sub>REP</sub> = repulsive energy. E<sub>CAV</sub> is the cavitation energy returned by the GAUSSIAN03 code (Pierotti-Reiss theory);  $\Sigma E$  = sum of electronic plus electrostatic and non-electrostatic (dispersion, repulsion) energy terms; ZPC = Zero Point Correction. Terms-U,H,G = thermal corrections to the internal energy (U), enthalpy(H) and Gibbs free energy (G); V<sub>CAV</sub> = cavitation volume in the dielectric continuum delimited by the Solvent Accessible Surface (SAS). H°<sub>f,298.15</sub>, S° <sub>298.15</sub> and G°<sub>f,298.15</sub> are the conventional enthalpy of formation from the elements, the conventional entropy and the conventional Gibbs free energy of formation from the elements at standard state (1-molal solution referred to infinite dilution) under electron convention, respectively. We refer to Vetuschi Zuccolini et al. (2011) for an outline of the procedures adopted to retrieve the conventional properties from the absolute ab-initio data. Values in brackets refer to the gaseous state (isolated ion).

Ion	[OH <sub>2</sub> ] <sup>0</sup>	[OH] <sup>0</sup>	[O] <sup>2-</sup>	[ <b>O</b> ] <sup>.</sup>	[ <b>O</b> ] <sup>0</sup>
Multiplicity	1	2	1	2	3
E <sub>SS</sub> (kJ/mol)	-25.65	-39.66	-941.36	-276.86	-1.42
E <sub>DISP</sub> (kJ/mol)	-20.04	-13.64	-17.53	-12.01	-8.58
E <sub>REP</sub> (kJ/mol)	5.73	2.09	20.33	6.86	2.26
E <sub>CAV</sub> (kJ/mol)	24.31	21.76	7.36	10.79	14.98
$\Sigma E$ (hartree)	-76.438682	-75.747572	-75.215684	-75.230500	-75.064849
ZPC (hartree)	0.020805	0.007333	-	-	-
Therm-U (hartree)	0.023640	0.009693	0.001416	0.001416	0.001416
Therm-H (hartree)	0.024584	0.010637	0.002360	0.002360	0.002360
Therm-G (hartree)	0.003139	-0.009646	-0.013915	-0.014569	-0.014952
$V_{CAV}$ (Å <sup>3</sup> )	47.206	26.522	5.277	12.508	24.429
H° <sub>f,298.15</sub> (kJ/mol)	-242.2 (-228.8)	10.4 (35.8)	-152.5 (778.6)	-185.2 (85.9)	255.9 (248.6)
S° <sub>298.15</sub> [J/(mol×K)]	188.8 (188.7)	178.6 (178.2)	143.3 (143.3)	149.1 (149.1)	152.4 (152.4)
G° <sub>f,298.15</sub> (kJ/mol)	-229.0 (-215.5)	7.2 (32.7)	-152.2 (779.0)	-192.8 (78.3)	241.0 (233.8)

As already seen in Figure 2, pure molten silica is the medium that exerts the lowest solute/solvent interaction among the investigated ones because of the relatively low numeral density. Still, non-negligible solute/solvent interaction energies affect significantly the bulk equilibrium constant  $K_{11}$ .

The energy terms involved in the ionic dissociation equilibrium 11-1 and in the proton-oxygen recombination in the dielectric cannot be fully appreciated because of the intrinsic difficulty of assigning the proper energy to the free proton in the medium (Vetuschi Zuccolini et al., 2011). However, the proton disappears in the bulk equilibrium and, for the sake of simplicity, we will assign to it a provisional zero value. Under this simplifying assumption, while the ionic dissociation (11-1) in the gaseous state would

require 994.5 kJ/mole, the effect of the reaction field is to reduce this energy to 76.8 kJ/mole. The depolymerization process 11-2 in the dielectric medium releases -474.5 kJ/mole while the same reaction between isolated moieties would be much more energetic (-856.1 kJ/mole). The protonation of the oxygen functional of the polymer chains in the dielectric medium (11-3) is not a spontaneous process (200 kJ/mole adopting a provisional zero value for the Gibbs free energy of formation of the proton in solution), although it is energetically favorable when occurring among isolated moieties (-45.6 kJ/mole). When arranged in an Arrhenius plot (Figure 10) the ab-initio  $K_{11}$  constants, computed respectively for isolated species and for species immersed in the dielectric, encompass the most relevant literature  $K_{X,11}$  values hitherto proposed on the basis of discrete observations.



**Figure 10:** Arrhenius plot of the homogeneous speciation constant  $K_{11}$ . Ab-initio  $K_{11}$  values among real species (red dashed lines) are compared with conditional constants  $K_{X,11}$  based on infrared spectroscopy. The solid gray lines and the red dots are the values of  $K_{11}$  at identity for the SOLWCAD dataset and the SiO<sub>2</sub>-H<sub>2</sub>O wet solidus (Ottonello et al., 2015).

On the same plot are superimposed the best  $K_{11}$  interpolants of the SOLWCAD populations (both, refined and raw data; volume effects neglected) and the  $K_{11}$  values bringing to identity the SiO<sub>2</sub>-H<sub>2</sub>O wet solidus.

The bias between conditional constants ( $K_{X,11}$ ) and thermodynamic constants  $K_{11}$  is due to HB stabilization of the molecular form OH<sub>2</sub> in solution. Because the ideal speciation model regression of Nowak and Behrens (1995) was selected as a reference frame to estimate the magnitude of the HB energy terms, the model returns [OH<sub>2</sub>] and [OH] relative abundances consistent with this ideal reference model (Figure 11). Increasing the entropy of reaction  $\Delta S_{X,11}$  (i.e. shifting upward in a subparallel way the Arrhenius  $\ln K_{X,11} = f(T^{-1})$  function within reasonable limits), we would have arbitrarily decreased the magnitude of the HB contribution without altering significantly the model results. In other words, the computation is virtually unaffected by the reference model.



**Figure 11**: Calculated H<sub>2</sub>O speciation in the investigated media (raw data). ( $\Box$ )molar fraction of hydroxyl functionals [OH]<sup>0</sup>; (o) molar fraction of molecular water in solution. The effect of 1 Log unit in the value of the conditional constant  $K_{X,11}$  is superimposed only for graphycal purposes as a eye guide.

#### 4.2 P,T limits of application

The realm of experimental observations concerning the  $H_2O$  saturation surface covers actually only limited P-T ranges. The entire database adopted in this study covers for instance equilibrium temperatures between 908 and 1858 K, corresponding in the reciprocal T-space of figure 10 to the range 0.0005 - 0.0011 K<sup>-1</sup>.

In-situ spectroscopic measurements of hydrated (Mg,Fe)SiO<sub>3</sub> glasses synthesized at pressure between 5 and 41 GPa revealed a dominant role of HB (manifested by the presence of distinct OH stretching bands between 2250 and 2600 cm<sup>-1</sup>) at pressures between 15 and 25 GPa. (Closmann and Williams, 1995). First-principles (DFT) molecular dynamics simulations performed using local spin density approximation (LDA) on hydrated  $MgSiO_3$  (Mookherjee et al., 2008) confirmed that while at low pressures [OH]° and [OH<sub>2</sub>] are the main species, at high pressure Si-O-H-O-Si polyhedral linkages, -O-H-O-H- chains and polyhedral edge decoration of  $[SiO_6]^{8-}$  octahedra are present as well (see also to this purpose Figure 9 in Closmann and Williams, 1995). A later firstprinciples investigation of the same kind was performed by Baigain et al. (2015) on a Model Basalt (MB) composition, and confirmed essentially the results of Mookherjee et al. (2008). I.e, with increasing pressure more oxygen gets bonded with hydrogen at the cost of isolated species and the mean H-O coordination rises progressively from 1 to a value exceeding 2 at pressures above 80 GPa. Evidently, a detailed IEFPCM investigation of the role of pressure on the magnitude of HB would be beneficial in a next future. At present we limit ourselves to state that, in the realm of pressures investigated in this study the simple Silver-Stolper model is more than adequate, which is testified by the fact that the two experimental observations at high-P (i.e. 3GPa) are almost perfectly centered on the raw-data interpolant (Figure 8).

#### 5. APPLICATION

Obviously, the best procedure would require applying the *ab-initio* calculations directly on a given discrete composition, without recurring to energy interpolation functions. However, this is not an easy task for most potential users. Moreover, the implicit functions operating on the various forms of energy involved in the process require the utilization of an iterative minimization procedure. Since the SPT-PCM procedure must be predictive, we must start the computation by assuming completely anhydrous system at the P,T conditions of interest, and procede as follows:

 compute the gas phase fugacity of H<sub>2</sub>O through an appropriate EOS (we adopt here the Kerrich-Jacobs EOS for pure H<sub>2</sub>O);

- 2. compute the number density, thermal expansion, compressibility and dielectric constant of the liquid;
- obtain the electrostatic interaction in the absence of HB contributions and the cavitation energy at T,P of interest;
- 4. compute the Henry's Law constant and the Gibbs free energy of solution and retrieve the molar amount of the molecular form in solution [OH<sub>2</sub>] per unit mole of melt (i.e. eqs. 17 to 22);
- 5. scale to a 1 O pfu basis and apply the conditional constant  $K_{X,11}$  to retrieve the amount of hydroxyl terminations in solution (eqs. 12-1,2,3);
- 6. sum up the two forms and re-scale to a unit mole of melt basis;
- 7. iterate the steps 2 to 6 up to convergency (4 to 7 steps are normally sufficient to achieve a convergency at the 0.0001 concentration level)
- 8. add the HB contributions to the electrostatic interaction and repeat once the steps 4 to 6.

Operating on a common laptop, the computation requires  $\sim 10$  sec for  $\sim 10^3$  samples<sup>4</sup>.

. Obviously, a much better match between observed and SPT-PCM application is achieved if a precise excess HB Gibbs free energy function is available for a particular sub-system of interest. However, without that information the procedure remains sufficiently predictive, and may be applied conveniently at an exploratory level. For example, one has, through the computation of Henryan solubility, gas phase fugacity and excess contributions, an approximate hint of the expected amount of bulk  $H_2O$  in solution by applying the simplified model to a simple anhydrous SiO<sub>2</sub> liquid (Figure 12) or to a "granitic" composition, such as AOQ (Figure 13) and fixing the P,T conditions of the system. The mean absolute error involved in this exercise is ~0.040 moles for the wet solidus (6 values; Figure 12; 0.017 with the refined model parameters) and ~0.019 for the AOQ melt (50 values; Figure 13; 0.009 with the refined model parameters).

<sup>&</sup>lt;sup>4</sup> A simplified (user-friendly) Fortran routine is available upon request to G.O.



**Figure 12**: Predictive properties of the SPT-PCM procedure concerning the SiO<sub>2</sub> wet solidus.. The  $\Delta H^{\circ}_{HB}$ ;  $\Delta S^{\circ}_{HB}$  and  $\Delta V^{\circ}_{HB}$  terms are those obtained by non linear minimization on the extended dataset (see caption to Figure 4). The general model excess terms are the following  $RK_{H} = -2.841 \times 10^{-1} \text{ eV}$ ;  $RK_{S} = 8.883 \times 10^{-8} \text{ eV/K}$ ;  $RK_{V} = -3.637 \times 10^{-9} \text{ eV/bar}$ . The refined parameters are  $RK_{H} = -7.595 \text{ eV}$ ;  $RK_{S} = -6.050 \times 10^{-6} \text{ eV/K}$ ;  $RK_{V} = -8.920 \times 10^{-8} \text{ eV/bar}$ .



**Figure 13**: Model performance for the AOQ granitic composition. The parameters of the sub-regular isometric AOQ model are listed in the caption to Figure 4. The regression parameters are the following: y=1.011 and  $R^2 = 0.981$  for the AOQ model (50 samples); y=1.024x and  $R^2 = 0.964$  for the general model. The mean absolute error in the estimated bulk amount of H<sub>2</sub>O per unit mole of melt is 0.019 with the general model parameters and 0.009 with the refined parameters:  $RK_H = -5.480 \times 10^{-2} \text{ eV}$ ;  $RK_S = 2.635 \times 10^{-7} \text{ eV}/K$ ;  $RK_V = -2.923 \times 10^{-8} \text{ eV/bar}$ .

As a final emblematic application of the type of calculations promoted in this study, we show the saturation hypersurface of the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system at liquidus (Figure 14). The liquidus loci were obtained with

the procedure described in Belmonte et al. (2017) with a discretization step of 0.01 on the composition and of 1 K on the temperature in the 1000-3000 T °C range (i.e.  $1 \times 10^9$  points for the liquid and for each of the solid phases known to nucleate in the system). The convex-hull technique returned 4644 equipotential points identifying the liquidus. These P-T-X compositions where then employed in the SPT-PCM analysis.



Figure 14: H<sub>2</sub>O saturation hypersurface for the MAS system at a confining pressure of 0.9 GPa.

According to our calculations the eutectic point of the system is located at  $SiO_2 = 0.643$ ,  $Al_2O_3 = 0.124$ , MgO = 0.233 and T = 1433 °C, not far from the experimental observations of Presnall et al. (1979) for an anhydrous melting at P = 0.93 GPa (i.e.  $SiO_2 = 0.597$ ,  $Al_2O_3 = 0.146$ , MgO = 0.257; run N. 116.5 in Table 2 of Presnall [1978], when projected on the MAS plane). This eutectic is fairly well representative of Mid-Ocean Ridge Basalts (MORB) generated at the cusp in the solidus where a Spinel-Peridotite assemblage has a transition to a Plagioclase-Peridotite assemblage. The cusp is theoretically compulsory according to

Schreinemakers rules (Schreinemakers, 1915a,b,c) and roughly occurs at P = 0.9 GPa and T = 1300 °C. Undoutedly, the fact that our eutectic occurs at a higher T is due to the missing amount of CaO, but, besides this discrepancy, the identification between calculus and experiments is quite appropriate. As we may see in Figure 14, due to the T minimum, at the eutectic we observe the highest amount of dissolved H<sub>2</sub>O (X<sub>H2O</sub> = 0.162 moles per unit mole of melt; corresponding to ~5.43 wt. per cent). When the liquid moves upward within the Earth's gravitational field, the eutectic temperature is progressively lowered to some extent (i.e. from T = 1703 K at P = 0.9 GPa to T = 1634 K at P = 100 MPa). More importantly, however, the amount of dissolved H<sub>2</sub>O for liquids produced at the true eutectic and along the cotectic lines reduces drastically (Figure 15). At room pressure the calculated amount (X<sub>H2O</sub> = 0.002 moles per unit mole of melt; corresponding to ~0.06 wt. per cent) is not far from what observed in MORB matrixes (i.e. 0.1-0.5 wt. per cent according to Hart and Nalwalk, 1970; Moore, 1970; Bryan and Moore, 1977). Accepting that the computed amount of water at room pressure is "normal" for a MORB, it follows that most part of water is released during the ascent.



**Figure 15**:  $H_2O$  at saturation along the cotectics of the MAS system at various confining pressures. Arrows on the dotted line indicate the P-T-X<sub>H2O</sub> trajectory followed during the ascent to the Earth's surface form the depth of origin (~30 km).

#### 6. CONCLUSIONS

The way a solute molecule such as [OH<sub>2</sub>] "sees" the solvent cannot be perceived through the sticks-and-balls representations so popular in literature but needs an accurate account of the polarization effects in solution. Through the IEFPCM model one has a precise perception of the polarization effects induced by the countercharges distributed on the Solvent Accessible Surface (SAS) (see Figure S.1 in Supplementary material). The higher the numeral density of the solvent, the more intense the polarization effect and the ensuing electrostatic interaction (Figure 1 and Figures S.2 in Supplementary material). The adoption of appropriate solvent radii (Ottonello and Richet, 2014) provides a continuous and derivable function of mean solvent parameters, bypassing thus the need of discrete *ab-initio* computations. When the solvent molecules become oriented in order to satisfy the geometric conditions necessary to realize HB with the [OH<sub>2</sub>] solute molecules (Figure 1), the magnitude of the electrostatic radius of the solvent is altered as well, modifying in a complex manner the solute-solvent interaction. However, the gain in HB is partly counterbalanced by a loss in electrostatic interaction and non excessively influent at the high thermal regimes of interest in this study, due essentially to strongly negative  $\Delta S_{HB}$  terms (Table 3 in Ottonello et al., 2015). Comparing the K<sub>11</sub> values obtained by calculus with the observational K<sub>X,11</sub> constant one sees how HB energy terms act in solution, leading to stabilization of the [OH<sub>2</sub>] molecule with respect to hydroxyl functional terminations [OH]° (Figure 3). Disregarding for simplicity the effects of HB, DFT/B3LYP calculations on quasi-species in the framework of the IEFPCM model indicate that the compositional effect of the liquid is basically due to the polarization properties of the continuum, and not to long range structural details as it is commonly assumed in literature (Table 2 and Figure 10). Thanks to the fact that the bulk solute/solvent interaction may be represented as a continuous function of the number density of the solvent (Figure 2; Ottonello and Richet, 2014; Ottonello et al., 2015), a solution model of general validity is proposed. The marginal effects of HB are translated into a standard state G°<sub>HB</sub> contribution plus an excess regular non isometric term dependent upon the bulk amount of H<sub>2</sub>O in solution and expanded over the intensive variables T and P. We obtain in

this way a better model performance (Figures 8, 12,13) and an homogeneous speciation consistent with observables (Figure 11).

The present investigation emphasizes once again the heuristic properties of Tomasi's PCM and the correctness of the Pierotti-Reiss Scaling Particle Theory, and confirms, as an ancillary result, the validity of the simple but smart assumptions anticipated long ago by Silver and Stolper (1985) and largely adopted in the current literature to explain empirically the observed homogeneous speciation on the basis of an ideal mixing of quasi-species. It also focuses the attention on the beneficial role of the SOLWCAD thermodynamic treatment in refining the humongous amount of experimental data existing about bulk  $H_2O$  solubility in silicate melts at discrete P,T conditions (Papale, 1997; Papale et al., 2006).

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### FIGURE CAPTIONS

**Figure 1**: HB effects in a polymerized melt. The net gain in stabilization at the athermal limit is  $E_{HB} \cong -44.5 \text{ kJ/mol}$  when molecular water [OH<sub>2</sub>] approaches a hydroxyl functional [OH]° of a singly-hydroxylated monomeric group, while it reduces to  $E_{HB} \cong -33.7 \text{ kJ/mol}$  for a doubly-hydroxylated monomeric group.

**Figure 2**: Bulk solute/solvent interaction and its various components, resolved for a silicate melts population deemed to be sufficiently representative of the natural compositional realm (Ottonello and Richet, 2014) and plotted against the number density of the solvent. Open symbols denote calculations carried out with  $\gamma_{el}$ =1.0945 instead of the nominal value  $\gamma_{el}$ =1.20 (filled symbols). The resulting electrostatic interaction is enhanced of roughly -10.9 kJ/mol, stabilizing further the molecular water in the silicate liquid. The bulk interaction energy may be represented through a linear regression over the number density  $E_{int}/(kJ \times mol^{-1}) = -20.803 - 834.71 \times (\rho/Å^3)$  with a sufficiently high correlation coefficient (R<sup>2</sup> = 0.8821).

**Figure 3**: nominal values of  $K_{11}$  computed with the SPT-PCM approach with different EOS for the gaseous phase, compared with the regression of Nowak and Behrens (1995) which is based on insitu IR observations.

**Figure 4**: SPT-PCM calculations for the AOQ granitic composition compared to the experimental observations of Holtz et al. (1992, 1995) The HB contributions are included as an additional term of the electrostatic interaction  $G_{HB}(eV) = \Delta H^{\circ}_{HB} - T \times \Delta S^{\circ}_{HB} + P \times \Delta V^{\circ}_{HB} + G_{HB,excess} = 1.831 \times 10^{-1} - 2.114 \times 10^{-7} \times T(K) + 6.329 \times 10^{-9} * P(bar) + X_{H2O} \times (1 - X_{H2O}) \times [-5.480 \times 10^{-2} - 2.635 \times 10^{-7} \times T(K) - 2.923 \times 10^{-8} \times P(bar)]$  with the first three terms resolved through inverse methods operating on an extended database (i.e. 970 samples) and the excess contributions obtained with a fine tuning based on the observations of (Holtz et al., 1992, 1995).

**Figure 5**: Arrhenius plot of the computed  $K_{11}$  constants returning the observed bulk fractional amount of  $H_2O$  in solution (970 samples; 1 O pfu basis). Neglecting volume effects, the best interpolant is  $lnK_{11} = 5.6585-5117.1/T$ . Regression lines for the SOLWCAD refined population (Papale et al., 2006) and for the AOQ composition are reported for comparative purposes. The gap with the conditional constant after Nowak and Behrens (1995) may be eventually expressed in terms of a mean value of productorials of activity coefficients (i.e.  $lnK_{\gamma}$  in figure).

**Figure 6**: Results of the SPT-PCM procedure applied to the 970 samples of the dataset assembled by Papale et al. (2006), applying  $\ln K_{11} = 5.6585-5117.1/T$  (raw data) and  $\ln K_{11} = 5.7094-5371.8/T$  (SOLWCAD refinement).

Figure 7: Ideal model biases at the various bulk fractional amounts of H<sub>2</sub>O component in solution.

**Figure 8**: Ab-initio vs SOLWCAD-refined and raw data populations (970 samples in each set). The simple regression for the sub-regular model is in both cases not far from the identity line, with a more marked dispersion when operating on the SOLWCAD-refined set, essentially due to the two outliers at P = 3 GPa. The inset shows the frequency distribution of the normalized error [difference]

between calculated and observed (or refined) value normalized to the observed (or refined) one] for the two polulations.

**Figure 9**: Effects of partial delocalization of H centers about the oxygen of  $[OH_2]$ : from an initial condition of complete localization, where 3 normal vibrational modes are present (blue circle) hydrogens become progressively localized on the O- centers of neighbouring polimeric units (red circles). The OH stretching motions becomes then progressively more intense.

**Figure 10:** Arrhenius plot of the homogeneous speciation constant  $K_{11}$ . Ab-initio  $K_{11}$  values among real species (red dashed lines) are compared with conditional constants  $K_{X,11}$  based on infrared spectroscopy. The solid gray lines and the red dots are the values of  $K_{11}$  at identity for the SOLWCAD dataset and the SiO<sub>2</sub>-H<sub>2</sub>O wet solidus (Ottonello et al., 2015).

**Figure 11**: Calculated H<sub>2</sub>O speciation in the investigated media (raw data). ( $\Box$ )molar fraction of hydroxyl functionals [OH]<sup>0</sup>; (o) molar fraction of molecular water in solution. The effect of 1 Log unit in the value of the conditional constant K<sub>X,11</sub> is superimposed only for graphic purposes as an eye-guide.

**Figure 12**: Predictive properties of the SPT-PCM procedure concerning the SiO<sub>2</sub> wet solidus. The  $\Delta H^{\circ}_{HB}$ ;  $\Delta S^{\circ}_{HB}$  and  $\Delta V^{\circ}_{HB}$  terms are those obtained by non linear minimization on the extended dataset (see caption to Figure 4). The general model excess terms are the following RK<sub>H</sub> = -2.841×10<sup>-1</sup> eV; RK<sub>S</sub> = 8.883×10<sup>-8</sup> eV/K; RK<sub>V</sub> = -3.637×10<sup>-9</sup> eV/bar. The refined parameters are RK<sub>H</sub> = -7.595 eV; RK<sub>S</sub> = -6.050×10<sup>-6</sup> eV/K; RK<sub>V</sub> = -8.920×10<sup>-8</sup> eV/bar.

**Figure 13**: Model performance for the AOQ granitic composition. The parameters of the subregular isometric AOQ model are listed in the caption to Figure 4. The regression parameters are the following: y=1.011 and  $R^2 = 0.981$  for the AOQ model (50 samples); y=1.024x and  $R^2 = 0.964$ for the general model. The mean absolute error in the estimated bulk amount of H<sub>2</sub>O per unit mole of melt is 0.019 with the general model parameters and 0.009 with the refined parameters:  $RK_H =$ -5.480×10<sup>-2</sup> eV;  $RK_S = 2.635 \times 10^{-7}$  eV/K;  $RK_V = -2.923 \times 10^{-8}$  eV/bar.

Figure 14: H<sub>2</sub>O saturation hypersurface for the MAS system at a confining pressure of 0.9 GPa.

**Figure 15**:  $H_2O$  at saturation along the cotectics of the MAS system at various confining pressures. Arrows on the dotted line indicate the P-T-X<sub>H2O</sub> trajectory followed during the ascent to the Earth's surface form the depth of origin (~30 km).