H/D isotopic interpretation of hydration isotherms

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Various methods have been developped since years for describing the poral distribution of porous materials from hydration isotherms measurements. The most well known is the BJH method, which relies on a model of cylindric pores. More recently, methods (e.g. Or and Tuller, 1999) consider pores with various geometries (slit pores, pores with polygonal section), providing great improvements in the description of hydration isotherms and/or retention curves.

However, these approaches are based on a series of assumptions (constant molar volume of hydration water, *a priori* geometrical characteristics of pores, no contact angle between adsorption film and capillary meniscus, etc). As a result, determination of the amount of water available for chemical reactions remains qualitative in such systems.

Richard *et al.* (2007) have measured the H/D isotopic fractionation factor (α) between hydration water and water vapor as a function of relative humidity (RH). Two main types of water were identified and interpreted as 2D (low RH) and 3D (high RH) water networks. The 3D-water is considered as the location where aqueous reactions occur.

Based on this work and without any *a priori* assumption on the pore space geometry, we propose a new approach aiming at quantifying the amount of "reactive" (capillary) water in a porous medium as a function of water saturation.

Given known values of the fractionation factors (α_f and α_c) for film (2D) and capillary (3D) waters, respectively (see fig. 1a), relative amounts of both types of water can be determined along the hydration isotherm (see fig. 1b) according to: $N\ \alpha = N_f\ \alpha_f + N_c\ \alpha_c$; with $N = N_f + N_c$; N, N_f and N_c are the amounts of total hydration, film, and capillary waters, respectively.

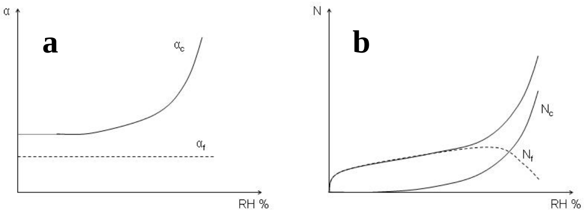

Figure 1: schematic representations of a) H/D fractionation factors and b) amounts of film and capillary water along a hydration isotherm, as a function of RH.

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A new version of the Fe-Ti-oxide thermo-oxybarometer relevant to basic magmatic rocks

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The Fe-Ti-oxide thermo-oxybarometer, which is based on equilibrium between coexisting Ilm_{ss} (ilmenite-hematite solid solution) and Tmt (magnetite-ulvöspinel solid solution) has been widely used to retrieve information on temperature and oxygen fugacity (fO_2) during magmatic and metamorphic processes. However, the two available formulations (Andersen & Lindsley, 1988; Ghiorso & Sack, 1991) yield unsatisfactory results at high temperature and low to moderate fO_2, i.e. in conditions relevant to crystallisation in basic rocks.

To contribute to a re-calibration of the Fe-Ti oxide thermo-oxybarometer, we have carried out synthesis and re-equilibration experiments in the systems Fe-Ti-O (Lattard *et al*. 2005) and Fe-Ti-Mg-Al-O at 1000 to 1300°C and a large variety of fO_2. The compositions of coexisting Tmt and Ilm_{ss} were derived by EMP analysis.

Our results show that the addition of Mg and/or Al in the concentration ranges that are usual in Fe-Ti oxides from basic magmatic rocks can be accommodated by simple projections in the range 800-1300°C under low to moderate fO_2 conditions. To generate an empirical formulation of the Tmt-Ilm_{ss} thermometer-oxybarometer for this T-fO_2 range we have performed numerical fits on an experimental data set comprising our results and those of selected literature studies (e.g. Evans *et al*. 2006). With the resulting expressions we can retrieve temperature values from X'_{usp} and X'_{ilm} (projected mole fractions) of Tmt-Ilm_{ss} pairs and fO_2 values from X'_{usp} and T.

We have tested our numerical formulations by using the compositions of Tmt-Ilm_{ss} pairs in products of liquidus experiments conducted at known T- fO_2 conditions in the frame of several literature studies (e.g. Toplis & Carroll, 1995). In most cases, the calculated values reproduce the experimental ones within ± 50°C and ± 0.4 log fO_2. This is a significant improvement compared to the previous models.

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