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Reduction of OH contamination in quantification of water contents using NanoSIMS imaging

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ABSTRACT

Quantification of water content is relevant in various topics in geology and planetary sciences. NanoSIMS has capabilities for high spatial resolution imaging and offers opportunities to accurately quantify water contents at fine scale on small surface areas. The main concern using ion microprobe techniques is to estimate and minimize contribution of water contamination, from residual gas in the sample chamber, sticking onto the surface of the sample. Here we tackle a set of sputtering/analytical parameters and we evaluate their relative influence on the OH^-/Si^- ratio. We demonstrate that a high erosion rate, reached using a primary beam intensity of ~25 pA, is sufficient to lower this OH contamination for basaltic glass. This leads us to describe a procedure to correct for OH contamination and thus determine accurate values of OH/Si ratio in order to quantify water contents in silicate materials using NanoSIMS imaging.

1. Introduction

Quantification of water content in minerals is of primary interest in geology and planetary sciences as water has a direct influence on the geodynamic and geochemistry of planets (Regenauer-Lieb, 2006). Numerous studies have focused on nominally anhydrous minerals. The first measurement of low water contents was reported by Martin and Donnay (1972) who suggested that water may occur as OH groups in minerals in the deep Earth. Water in the mantle plays a key role in its properties like hydrous melting (Hirschmann, 2006), rheology (Hirth and Kohlstedt, 1996) and electrical conductivity of minerals (Huang et al., 2005). All of these applications require accurate measurements of water content in minerals.

Bulk analyses like the hydrogen manometry or thermogravimetric analysis cannot provide information on the spatial distribution of water at fine scale. Therefore, other methods were investigated using microbeam techniques for quantification of hydrogen concentration in nominally anhydrous minerals. Nuclear reaction analysis, rutherford backscattering spectrometry and energy recoil detection analysis offer some advantages like depth profiling of H (Reiche et al., 2006). They are also insensitive to matrix effects and are absolute methods making quantitative analyses easier (Lanford, 1992). However, these methods are suitable only for water content >0.1 wt.% (Bureau et al., 2003). Infrared spectroscopy (FTIR) remains the most commonly used method to detect and analyse hydrous components with a detection limit of a few ppm of H_2O, but at the cost of a complex sample preparation, involving thin and double polished sections. However, since the first studies of H_2O contents in geological materials, SIMS related techniques have been shown to produce reproducible and accurate in situ analyses (Hinthorne and Andersen, 1975; Delaney and Karsten, 1981). Moreover, comparing SIMS with FTIR, Koga et al. (2003) concluded that the relatively simple analytical geometry and the high spatial resolution of SIMS offer considerable advantages for measurements of low hydrogen concentration. SIMS is thus broadly used in geological and planetary sciences where quantification of water content is often associated to hydrogen isotope studies in order to address the origin of water in meteorites (Deloule et al., 1998) or, more recently, in lunar rocks (Greenwood et al., 2011) and soils (Liu et al., 2012).

Marked improvements have resulted in the analytical ability to measure hydrogen concentration at low levels (Rossman, 2006). The challenge to measure accurately low water contents in silicate-based materials using SIMS results from the presence, in the sample chamber, of residual H-bearing gases, even under the ultra-high vacuum of ion probes, responsible for H background signal. Magee and Botnick (1981) showed that H background intensity in H analysis is due to efficient adsorption of H_2O on silicon sample. Experimental protocols have been developed to minimize this H background signal and enhance accuracy and reproducibility during SIMS analysis (Hauri et al., 2002; Koga et al., 2003; Aubaud et al., 2007). These experimental

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protocols require heating and degassing of the sample (Ottolini et al., 1995), baking sample chamber to improve ultrahigh-vacuum, using resin-free mounting techniques (Demouchy et al., 2005), using energy filtering method (Hervig and Williams, 1988; Deloule et al., 1995), presputtering the surface until a steady state regime is attained and sputtering a larger area than the collected spot (Yurimoto et al., 1989). Furthermore, improvements related to bombardment conditions have been achieved. Hence, Wittmaack (1983) noted that high erosion rates constitute a prerequisite for low background levels in depth profiling studies involving H. Recently, some authors have demonstrated the influence of primary ion beam intensity on the H^+/Si^+ ratio (Rhede and Wiedenbeck, 2006; Ludwig and Stalder, 2007).

During the last decade, NanoSIMS opened up a new era of studies of light element distribution, by combining high mass resolution with fine scale imaging capabilities (Hoppe, 2006). Consequently, authors have demonstrated recently the accuracy of water content measurement using NanoSIMS in the study of lunar rocks (Hauri et al., 2011; Barnes et al., 2013; Saal et al., 2013; Tartèse et al., 2013) and terrestrial minerals (Levi-Setti et al., 1984; Mosenfelder et al., 2011). It must be noted that imaging water content with the NanoSIMS requires rastering, e.g. scanning the primary ion beam over the sample surface. Thus, contamination deposit occurs between each passage of the beam. This results in markedly different settings than usual methods developed on regular ion probes (Hauri et al., 2002). This study is dedicated to test the ability of the NanoSIMS ion probe to the study of water distribution in silicates at small scales, with a special emphasis on bombardment conditions. To this end, we acquired a large set of analyses on a silicate glass standard. We aim at understanding the OH^-/Si^- ratio behaviour under a large variety of analytical parameters, including primary beam intensity, counting time and surface area. As a result, a method is presented in order to perform accurate analyses and to minimize in situ hydrogen contamination contribution.

2. Material and methods

2.1. Sample preparation

The DR15-2-5 basaltic glass, from Southern Indian Ridge (SWIR), was imaged with the Cameca NanoSIMS 50 installed at the Museum National d'Histoire Naturelle of Paris, France. The chemical composition of this glass is reported in Table 1. The sample was mounted in a way to reduce the amount of epoxy: a hole was drilled in a 10 mm aluminium disk with a 2 mm diameter drill bit. In the hole, the sample was mounted individually with a very small amount of epoxy and then polished successively with 1 and 0.25 μm diamond paste to produce a planar surface. The mount was then cleaned in an ultrasonic bath of ethanol and then gold-coated (thickness 20 nm). The sample was introduced in the airlock one week before the analytical session I to let it outgas, so the total vacuum pressure in the analysis chamber during the measurements remained below 5.0×10^{-10} Torr (6.7×10^{-10} mbar). Another session (session II) was required and vacuum pressure reached 1.5×10^{-9} Torr (2.0×10^{-9} mbar). Different image parameters were used along the two sessions: in session I, images were performed onto 20 × 20 surface area and in session II, we varied the surface area. Because of this discrepancy of vacuum pressure, sessions I and II are not comparable.

2.2. Analytical settings

$^{16}O^{1}H^-$ and $^{28}Si^-$ secondary ions were imaged by scanning ion imaging with the NanoSIMS 50. Analyses were performed with a 16 keV Cs^+ primary ion beam rastering the surface of the sample. Four primary beam intensities were used to perform analyses: 1.2, 7, 14 and 23 pA with a D1-3 (200 μm) aperture diaphragm. Beam sizes for these primary beam intensities were roughly between 120 nm and 500 nm, respectively, for 1.2 pA and 23 pA. For each beam intensity, analysed areas were 5×5 μm^2 and 20×20 μm^2, divided in 64 × 64 pixels and 256 × 256 pixels, respectively. Presputtering was achieved with a primary beam of 335 pA using a D1-1 (750 μm) aperture diaphragm with a duration and a surface depending on the analysed surface area. A presputtering on a 25×25 μm^2 surface area during 15 min was performed before 20×20 μm^2 images; 5 min of presputtering on 7×7 μm^2 surface area before 5×5 μm^2 images. Presputtering was performed to remove coating and initial surface contamination and to reach the sputtering steady-state regime. The duration of measurement by pixel also varied from 1 to 20 ms/px only for the 20×20 μm^2 images for each primary beam intensity. The number of cycles depended on the counting time and surface areas: varying from 5 to 50 cycles to get at least 30 min for each analysis. The set of analyses is shown in Table 2. An electron flooding gun was used for charge compensation with a beam intensity of 500 nA using a D1-3 (200 μm) aperture diaphragm. Data were processed with the L'IMAGE software developed by Nittler and Alexander (2003). The deadtime was set at 44 ns and corrected with the L'IMAGE software. Statistic treatment of the chemical ratio was performed by dividing each image in 25 ROIs (region of interest) of 3.12×3.12 μm^2 surface area, as edges of images are discarded. The mean of these 25 ROIs is representative of the image heterogeneity at low primary beam intensity. The mean of these ROIs was kept as the value for the measurement. Error was calculated using standard deviation over these 25 ROIs.

3. Results

We have tested the influence of (i) analysed surface area, (ii) primary beam intensity and (iii) counting time on OH^-/Si^- ratios. External reproducibility of OH^-/Si^- ratio is 3% for the session I.

Fig. 1 shows that the OH^-/Si^- ratio mainly depends on the analysed surface area based on measurements of the session II (Table 2). This dependence is stronger at low primary beam intensity: we observe a factor 4.2 between the 5×5 μm^2 and 20×20 μm^2 images using 1.2 pA. It is however much less sensitive for higher primary beam intensity. Consequently, all analyses have to be performed with the same surface area to be processed together and compared. Note that measurements of session II are only taking into account here and that we do not compare measurements of the two sessions because of the large variation of the vacuum pressure in the analysis chamber between session I and session II. The variation of the pressure vacuum affects the OH background and thus OH^-/Si^- ratios which vary from 0.714 ± 0.05 to 2.34 ± 0.43 (measurements made at 1.2 pA and on 20×20 μm^2 surface area) for session I to session II, respectively (Table 2). Thus, in the following text, measurements of session I will be considered.

Focusing on 20×20 μm^2 surface areas, the OH^-/Si^- ratio is plotted in Fig. 2 against primary beam intensity and counting time: OH^-/Si^- ratio decreases with increasing primary beam intensity until it reaches

Table 1
Chemical compositions of DR15 glass basaltic standard.

Sample	SiO_2 (wt%)	TiO_2 (wt%)	Al_2O_3 (wt%)	Cl (ppm)	FeO* (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na_2O (wt%)	K2O (wt%)	P_2O_5 (wt%)	H_2O (wt%)	Total (wt%)	
DR15-2-5 glass	50.81	1.82	14.78	160	11.15	0.2	6.95	10.37	3.1	0.46	0.21	0.2581	99.85	Clog (phd.2011)