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Progress in the determination of water in glasses and melt inclusions with Raman spectroscopy: A short review

Fortschritt in der Bestimmung von Wasser in Gläsern und Schmelzeinschlüssen mittels Raman-Spektroskopie: Ein Kurzbericht

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key words: Raman spectroscopy, water determination, comparator technique, melt inclusions

Zusammenfassung

Die „Komparator-Technik", die einen wesentlichen Fortschritt in der Bestimmung von Wasser in Gläsern und Schmelzeinschlüssen mittels Raman-Spektroskopie darstellt, steht im Mittelpunkt des Kurzberichtes. Der Wassergehalt wird einfach durch Vergleich mit einer Referenzprobe ermittelt. Durch diese Technik ist eine Kalibrierung nicht mehr notwendig. Weiterhin kann mit dieser Technik der Wassergehalt von Schmelzeinschlüssen bestimmt werden, die sich im Volumen weit von der Oberfläche entfernt in einer Mineral-Matrix befinden. Das ist insbesondere für sehr wasserreiche Schmelzeinschlüsse wichtig, da diese an der Oberfläche spontan Wasser abgeben würden.

Abstract

This paper is focused on the progress in the determination of water in glasses and melt inclusions with Raman spectroscopy. Using the presented "Comparator Technique" the water content of a sample is determined by simple comparison with a known standard. A calibration curve is not necessary. Furthermore, with this technique the water concentration in silicate melt inclusions can be determined without exposing the inclusions for measurements. This is very important for extremely water-rich melt inclusions, which would loose H_2O on exposure.

The latest developments in the determination of water with Raman spectroscopy

Our understanding of the behavior of volatiles in silicate melts has been closely linked to the development of the experimental and analytical methods used to investigate them (IHINGER et al. 1994). In this contribution, we show that the high spatial resolution and accuracy of Raman spectroscopy make it an important microanalytical technique for quantifying water in natural and experimental glasses.

Prior to 1999 microRaman spectroscopy had not been applied to the quantitative determination of water dissolved in silicate melts or glasses, although otherwise used extensively (e.g., BURKE, 2001), for the identification of daughter minerals in inclusions, as well as in structural studies of volatile-containing glasses (see IHINGER et al. 1994). Recently, the determination of water in natural glasses using confocal microRaman spectroscopy has developed into an established, routine analytical method (THOMAS, 2000 and 2002; THOMAS et al. 2005, 2006a; CHABIRON et al. 2004; ZAJACZ et al. 2005; BEHRENS 2006; DI MURO et al. 2006). This technique can be used for accurate and rapid determination of the total water content of glasses with high precision (<10%) over a wide concentration range (i.e., from 0.1 to over 35 mass% (~50 mol% H_2O)), however, the lower detection limit remains un-explored. With some reservation (see BEHRENS et al. 2006), quantitative determinations of the speciation of water (H_2O_m/OH) (CHABIRON et al., 2004; DI MURO et al. 2006) and of heavy water (D_2O_m/OD) (THOMAS et al, 2006a) are also possible.

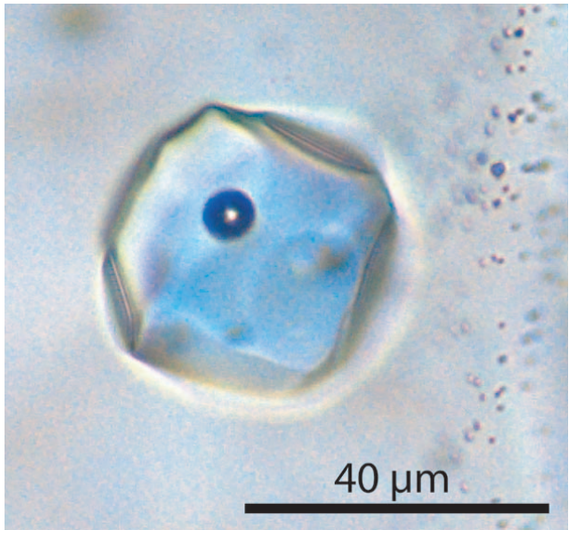
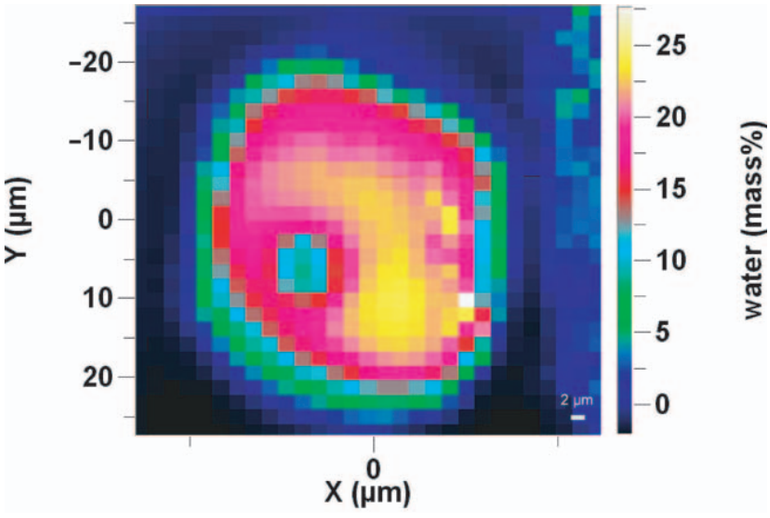


Fig. 1: (a) shows a water-rich (25 mass%) melt inclusion in pegmatite quartz from Ehrenfriedersdorf, re-homogenized at 600 °C and 1 kbar using the cold-seal pressure vessel technique with CO_2 as pressure media.
(b and c) The 2D and 3D diagrams of the water distribution in this MI. The distribution image was taken with the confocal high resolution Raman device LabRam HR800 (488 nm excitation Laser line and a 50 µm pinhole). The images are composed of 750 single 2 µm points. For each point there is a complete Raman spectrum in the 2800 to 4000 cm^{-1} frequency range. For the quantification of the water we used the integral intensity of the broad asymmetric H_2O–OH Raman band between 3100 and 3750 cm^{-1} and the calibration procedure given in THOMAS et al, 2006. The yellow color corresponds to 25 mass% water and the dark green color at the base corresponds to about 0 mass% water in the quartz matrix. The blue ridge at the right side comes from a small secondary fluid inclusion trail almost perpendicular to the quartz chip.



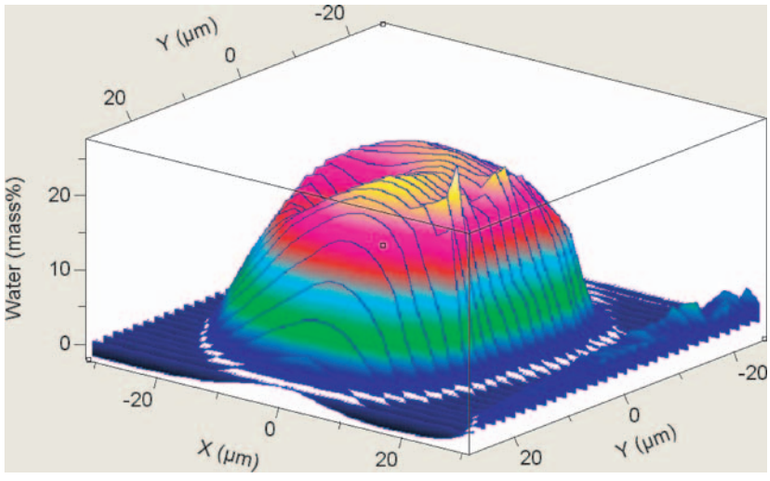
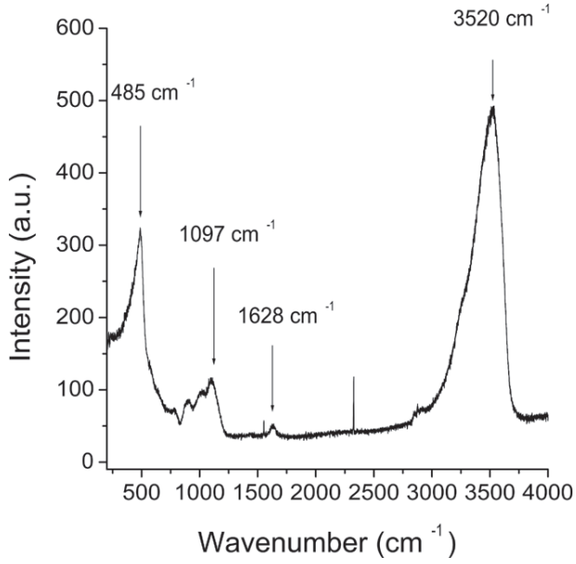


Abb. 1: In a ist ein wasserreicher (25 Ma%) Schmelzeinschluss im Pegmatitquarz von Ehrenfriedersdorf abgebildet. Dieser Einschluss wurde vor der Messung in einer Druckapparatur bei 600 °C und 1 kbar re-homogenisiert. Als Druckmedium diente CO_2. In b und c ist die Wasserverteilung in diesem Einschluss als 2D bzw. 3D Diagram dargestellt. Diese Verteilungsbilder wurde mit dem konfokalen, hochauflösenden Raman Spektrometer LabRam HR800 aufgenommen (Laser-Wellenlänge: 488 nm, 50 µm Pinhole). Die Bilder sind aus 750 einzelnen Messpunkten mit einer Größe von 2*2 µm aufgebaut. Jeder Messpunkt repräsentiert jeweils das komplette Raman Spektrum im Frequenzbereich von 2800 bis 4000 cm^{-1}. Für die Quantifizierung des Wassers verwendeten wir die Integralintensität der breiten asymmetrischen H_2O–OH Raman Bande im Bereich von 3100 und 3750 cm^{-1} und die in THOMAS et al. 2006a vorgestellte Kalibration. Die gelbe Farbe entspricht 25 Ma% und die dunkelblaue Farbe der Basis 0 Ma% Wasser. Der blaue bis grüne Rücken auf der rechten Seite resultiert von kleinen sekundären Flüssigkeitseinschlüssen, die senkrecht im Quarzschliff verlaufen.

Fig. 2a: Raman spectrum of albite glass (glass AB84 with 11.95 mass% H_2O; see THOMAS, 2000) between 200 and 4000 cm^{-1}. The broad band in the 485 cm^{-1} region results from the T–O–T symmetric bending mode. The bands centred at about 1090 cm^{-1} represent T–O and T–O–T bending and stretching modes, the weak band at 1628 cm^{-1} corresponds to H–O–H bending vibrations of molecular water dissolved in the glass. The broad and asymmetric band at 3520 cm^{-1} represent molecular water and hydroxyl groups in the glass.

Abb. 2a: Das Raman-Spektrum eines Albit-Glases (Glas AB84 mit 11.95 Ma% Wasser; vgl. THOMAS 2000) im Freuenzbereich zwischen 200 und 4000 cm^{-1}. Die breite Bande bei 485 cm^{-1} resultiert vom symmetrischen bending Mode. Die Banden um 1090 cm^{-1} repräsentieren T–O und T–O–T bending und stretching Moden, die schwache Bande bei 1628 cm^{-1} entspricht den bending Schwingungen des im Glas gelösten molekularen Wassers. Die breite und asymmetrische Bande bei 3520 cm^{-1} repräsentiert molekulares Wasser und Hydroxylgruppen im Glas.



The newest generation of Raman spectrometers (e.g., the LabRam HR UV) permits the collection of H_2O-concentration profiles, for example diffusion profiles in glasses, and determination of H_2O-distribution in melt inclusions, with a high spatial and concentration resolution. Lateral resolution of about 1 μm, possible with the confocal technique, makes feasible the study of small objects like melt inclusions in rock-forming minerals (quartz, plagioclase, olivine etc.). For example, in a pseudo-holographic Raman map for H_2O, each 2 μm point contains a complete quantitative Raman spectrum for H_2O (figure 1a–c).

The advantage of Raman spectroscopic technology in the study of melt inclusions over traditional infrared spectroscopy (FTIR), another very important vibrational spectroscopic technique, lies in the simplicity of sample preparation, the great concentration range, and the ability to selectively analyze discrete volumes within the sample, as well as the lack of matrix dependence of this technique. As applied to melt inclusions, this means the H_2O content of glasses can be determined for granitic to basaltic compositions (see figures 2a–c). Moreover, prior knowledge of the composition and density of the analysed glasses is no longer required for these determinations.

Although largely overlooked, the Raman signal in the frequency region from 2800–4000 cm^{-1} is directly proportional to the H_2O_T concentration. Since the integral intensity increases linearly with the concentration, quantification by normalizing the (H_2O+OH) band intensity with the low wavenumber band (T–O–T bending band near 500 cm^{-1} or the T–O stretching band near 1000 cm^{-1}) is un-necessary. This very important fact emphasized recently (THOMAS et al. 2006a) results in a very simple, exact and matrix independent method: the "Comparator Technique" for the determination of H_2O. Only a pair of reference samples for comparison purposes is needed for the complete concentration range. In the simplest case only a single reference glass is needed. In this way, the analytical determination of H_2O by Raman spectroscopy is drastically simplified. Thus, the Raman technique for the quantitative determination of H_2O becomes the method of choice.

The another advantage of the confocal microRaman technique over other techniques is that the H_2O content of melt inclusions can be determined for inclusions located below the sample surface. Only this method permits the study of H_2O-rich, unstable glasses/inclusion glasses which would be destroyed by spontaneous and irreversible decomposition during sample preparation (THOMAS et al. 2006a).

During the study of H_2O-rich melt inclusions in pegmatite minerals we demonstrated that complete miscibility between pegmatite melts and H_2O exists above 700 °C and about 1 kbar (THOMAS et al. 2006b). Furthermore, we have found inclusions with up to 70 mass % H_2O, in addition to the melt inclusions which characterize the solvus boundary. According to their physico-chemical behavior, these other H_2O-rich inclusion type can be interpreted as high temperature gel inclusions. These findings were only possible with the development of this

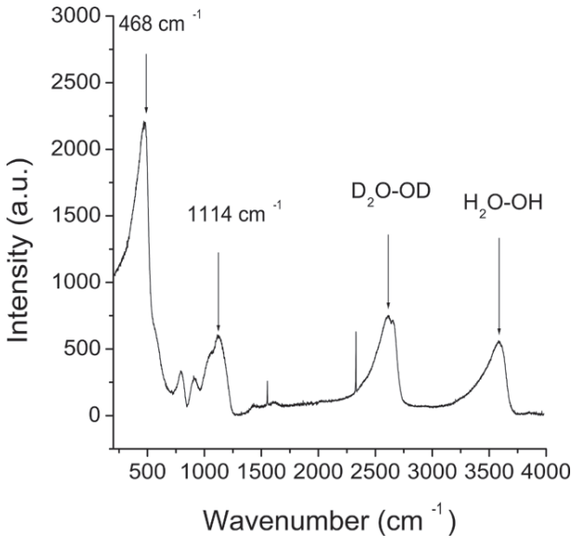


Fig. 2b: Raman spectrum of a rhyolitic H_2O and D_2O bearing reference glass (about 5 mass% of each) with the both characteristic broad asymmetric H_2O–OH and D_2O–OD stretching band between 3100 and 3750 cm^{-1} and about 2250 and 2900 cm^{-1}, respectively (see THOMAS et al., 2006a).

Abb. 2b: Raman Spektrum eines H_2O und D_2O haltigen rhyolitschen Glases (jeweils etwa 5 Ma%) mit den beiden charakteristischen breiten asymmetrischen H_2O–OH und D_2O–OD stretching Banden zwischen 3100 und 3750 cm^{-1} und 2250 und 2900 cm^{-1} (vgl. THOMAS et al. 2006a).

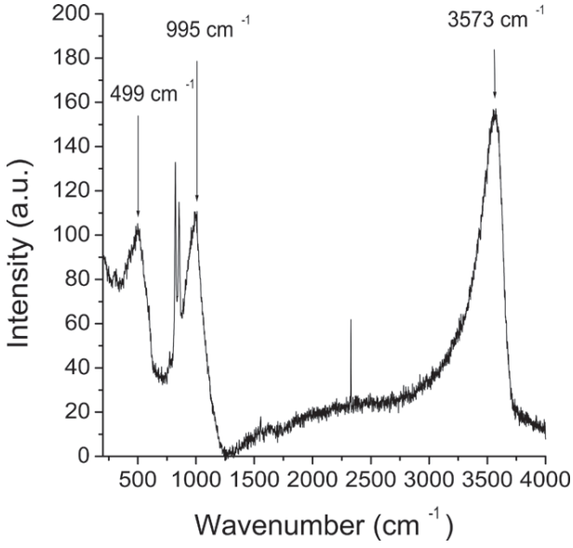


Fig. 2c: Raman spectra of a basaltic glass in a melt inclusion in olivine from the Chikurachki Volcano, Kuril arc, Russia with 6 mass% H_2O_T. The sharp bands at 824 and 856 cm^{-1} are characteristically for forsterite-rich olivine of the inclusion matrix. The strong band at 3573 cm^{-1} represent molecular water and hydroxyl groups in the inclusion glass.

Abb. 2c: Raman Spektrum eines Schmelzeinschlussglases mit basaltischer Zusammensetzung im Olivin vom Chikurachki Vulkan, Kurilen, Russland mit einem Gesamtwassergehalt (H_2O_T) von 6 Ma%. Die scharfen Banden bei 824 und 856 cm^{-1} sind für Forsterit-reichen Olivin der Einschlussmatrix charakteristisch. Die starke Bande bei etwa 3573 cm^{-1} repräsentiert molekulares Wasser und Hydroxyl-Gruppen im Einschlussglas.

Raman method. The study of these inclusions opens a new window in colloid research and economic geology, since such phases have the potential to extract, store, and transport, large quantities of trace and ore-forming elements. Additionally, such phases may be very effective ion exchange media. This new development in Raman spectroscopy for the determination of the H_2O in glasses gives a fresh impetus to the experimental petrology.

Finally we want to emphasize here that the comparator technique can be used also advantageously for the quantitative determination of other components like H_3BO_3, HCO_3^- and CO_3^{2-} in fluid inclusions.

Conclusions

The "Comparator Technique" strongly simplifies the analytical possibilities of confocal micro-Raman spectroscopy for the determination of water in glasses and melt inclusions from 0.1 to over 35 mass%. We can determine the water concentration of unexposed inclusions in a matrix non-destructively and with high precision, and construction of a calibration curve is un-necessary, it is much easier to determine the total water content of a sample directly against a reference glass of known water content. Given the non-destructive nature of the determination,

minimal sample preparation, and the simplicity, this new technique has considerable advantages.

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