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研究課題名（和文）Creating glass standards for SIMS analysis of H2O and CO2 in rhyolite glass

研究課題名（英文）Creating glass standards for SIMS analysis of H2O and CO2 in rhyolite glass

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研究成果の概要（和文）：本申請研究課題では、流紋岩に含まれるH2OおよびCO2濃度を二次イオン質量分析装置（SIMS）により精度・確度良く分析する際に必須の標準試料を作成することを目的とした。SIMS分析のための標準試料として天然および合成ガラス試料を準備し、フーリエ変換赤外分光光度計（FTIR）を用いてH2OおよびCO2濃度を決定した。これらの標準試料作成により、流紋岩に含まれる揮発性元素濃度をより正確に定量することが可能になった。したがって、これらの標準試料を今後の研究に活用することで、流紋岩質マグマの脱水および水和プロセスの解明などに寄与することが期待される。

研究成果の概要（英文）：This research will create essential calibration standards for SIMS analyses of H2O and CO2 in rhyolite. Standards will include natural and synthetic glasses, selected following FTIR analysis of their volatile distributions. These standards will enable current and future studies of volatiles in rhyolite glasses, and data obtained during their characterization will also yield insights into degassing and hydration processes.

研究分野：　Volcanology

キーワード：　glass standards　FTIR　SIMS　volatiles

## １．研究開始当初の背景

Volcanic eruptions are driven by magmatic degassing of volatiles such as $H_2O$ and $CO_2$. Measurements of the dissolved $H_2O$ and $CO_2$ contents of glasses within erupted volcanic rocks or high pressure and temperature laboratory experiments can therefore help us to investigate magmatic and eruption processes. Two key methods for measuring $H_2O$ and $CO_2$ in volcanic glasses are Secondary Ion Mass Spectrometry (SIMS) and Fourier Transform Infra Red (FTIR) spectroscopy. Both of these methods require glass standards with known concentrations, whose composition is similar to that of the sample to be analysed. In order to investigate degassing of silica-rich magma compositions, which have the potential to produce highly explosive eruptions, it is necessary to have standard glasses of $H_2O$ and $CO_2$ for rhyolite composition.

## ２．研究の目的

The key objective of this research was to create calibration standards for SIMS analyses of $H_2O$ and $CO_2$ in rhyolite. Standards with high concentrations need to be synthesized with high pressure and temperature experiments. In doing so, a secondary objective was to utilize pressure and temperature conditions that would provide new data on volatile solubility. Additional objectives were to investigate secondary hydration processes and calibration of the 1830 $cm^{-1}$ Si-O peak in FTIR spectra for finding sample thickness.

## ３．研究の方法

Originally it was planned to use glasses from previously erupted material as the low concentration standards. However, increasing recognition that even nano-scale crystals and other variations within natural glasses can cause problems for microanalytical techniques led to a decision to use laboratory synthesized glasses instead, which also increased the number of solubility data that could be collected. A natural obsidian was used as a starting material. For low concentration standards this was synthesized at pressures and temperatures of up to 25 MPa and 850 °C in cold-seal apparatus at Tohoku University, in collaboration with Michihiko Nakamura and Satoshi Okumura. For high concentration standards the starting material was synthesized at up to 770 MPa and 1000 °C in high pressure internally heated pressure vessels (IHPV) at Tokyo Institute of Technology, in collaboration with Akihiko Tomiya and Masashi Ushioda. After synthesis, these glasses were analysed by imaging FTIR to ascertain the concentration and homogeneity of the volatile distribution. Further confirmation will come from additional manometry analyses. Glass pieces were then mounted in indium for use in SIMS analyses.

## ４．研究成果

Synthesized glasses span a wide range of $H_2O$ and $CO_2$ contents, which can be added to previously published volatile solubility data for the same glass composition. Following additional measurements they will be made into indium mounts for SIMS and made available for loan to other

researchers. A preliminary test SIMS calibration of a few standard glasses for analysis of submarine silicic glasses previously analysed by FTIR identified an unexpected offset in areas of glass affected by secondary hydration, i.e. with elevated ratios of molecular $H_2O$ to hydroxyl (OH) groups. The cause of this interesting phenomenon is still being investigated, and is expected to inform our understanding of the hydration process and glass structure. FTIR spectra of glasses have also been used to investigate controls on the position and heights of Si-O absorption peaks, and a manuscript is being prepared on their use for identifying glass composition and thickness.

## ５．主な発表論文等

〔雑誌論文〕（計１件）

① I.M. McIntosh, A.R.L. Nichols, K. Tani, and E.W. Llewellin (2017) *Accounting for the species-dependence of the 3500 $cm^{-1}$ $H_2O_t$ infrared molar absorptivity coefficient: implications for hydrated volcanic glasses* American Mineralogist, 102, 1677-1689, Peer-reviewed.

〔学会発表〕（計６件）

① I.M. McIntosh *Creating rhyolite glass volatile standards, with application to understanding silicic submarine volcanism* Geological Survey of Japan seminar, 2018, Tsukuba, Japan

② I.M. McIntosh, A.R.L. Nichols, K. Tani and E.W. Llewellin. *Accurately measuring $H_2O$ in volcanic glasses: application of a new FTIR spectroscopy method.* International Association of Volcanology and Chemistry of the Earth's Interior, 2017 meeting, Portland, USA

③ I.M. McIntosh, A.R.L. Nichols, K. Tani and E.W. Llewellin. *Investigating submarine eruptions using $H_2O$ contents of volcanic glasses: application of a new FTIR spectroscopy method.* Japan Geoscience Union, 2017 meeting, Makuhari Messe, Japan

④ I.M. McIntosh, K. Tani, A.R.L. Nichols, F. Ikegami, R.J. Carey, O. Ishizuka, and Shipboard scientific groups of NT07-15, NT12-19, KS-13-3, and KS-16-6 cruises *Oomurodashi volcano: overview of an active shallow submarine silicic volcano in the northern Izu-Bonin Arc* Chapman Conference on Submarine Volcanology, 2017, Hobart, Australia

⑤ I.M. McIntosh, A.R.L. Nichols, K. Tani, E.W. Llewellin, C.I. Schipper, R. Stewart *Accurate measurement of $H_2O$ concentration and speciation in silicate glasses using FTIR* Japan Geoscience Union 2016 meeting, Makuhari Messe, Japan

⑥ I.M. McIntosh, A.R.L. Nichols, K. Tani, and E.W. Llewellin *Reconstructing final $H_2O$ contents of hydrated rhyolitic glasses: Insights into $H_2O$ degassing and eruptive style of silicic submarine volcanoes*

Goldschmidt 2016 meeting, Yokohama, Japan

## ６．研究組織

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