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Volatiles in merrillite from martian meteorite Tissint

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Abstract

We report new Cl and H isotopic data from Tissint – a martian meteorite of olivine-phyric shergottite type. Our data indicate that merrillite may accommodate up to 32 ppm of Cl, potentially representing the upper limit of Cl that can be accommodated in this nominally Cl-free phosphate. The δD values range from 721 ± 35 ‰ to 3496 ± 31 ‰, while the H_2O content is relatively modest (962 to 2341 ppm); the latter is much lower than previously reported values (all >5000 ppm), possibly representing either contamination from terrestrial environment or during sample preparation [1]. The measured δD range is possibly related to interaction of Tissint with surficial reservoirs on Mars (interaction with crustal fluids or the martian atmosphere) and/or influence of magmatic degassing.

1. Introduction

We report new Cl and H isotopic data from the martian meteorite Tissint; a well characterized depleted olivine-phyric shergottite which has been studied for its mineral chemistry, geochemistry, and shock metamorphism [2,3,4,5]. Recently, much attention has been paid to the isotopic studies and in particular that of Cl and H in merrillite from Tissint [1,6]. The overall goal of this study was to analyse the Tissint`s merrillites, which typically form at the very late stage of magma crystallization, and represent the major host of volatiles, which may provide important clues about the history of volatiles and other associated processes operating in Martian environment.

1.1 Material-Analytical Methods

Three polished thin sections were carefully examined using optical reflected light microscopy for the overall texture and mineralogy. X-ray mapping, measurement of mineral composition and detailed textural characterization of phosphates were performed for the three polished thin sections using a JEOL JXA-8900 Superprobe electron probe micro-analyzer at the laboratory of Mineralogy and Geology, Agricultural University of Athens. Mineral standards used were: quartz (Si), forsterite (Mg), corundum (Al), diopside (Ca), ilmenite (Ti, Mn), K-feldspar (K), albite (Na), fayalite (Fe), apatite (P), at 15 kV, 15 nA, 20 sec on peak counting time, 10 sec for each background, and a beam diameter 3-5 μm. For the element maps employed to locate phosphates we used the following conditions: 15 kV, 50 nA, 100 dwell time, 2-8 μm step size and ~1μm focused beam. The merrillite isotopic analyses and the determination of the water content was performed using a Cameca NanoSIMS 50L at the Open University, UK.

2. Nano-SIMS protocol

For the NanoSIMS analyses we followed the protocol which is extensively described in [7,8], with the following modifications:

- Once in the airlock, the first sample that was analysed for Cl was left to degas under vacuum at ~55 °C for 3-4 hours, while the second one (which has been analysed for H too) for 6 hours before transferring it to the vessel chamber.
- For analysis, the beam current was 90 pA for the Cl analyses, while 600 pA was used for H.
- For Cl analysis, the raster area was 7 μm × 7 μm. For H analyses the raster area was 10 μm × 10 μm with 25% electronic gating set in order to collect only secondary ions emitted from the central zone (5 μm × 5 μm) of the analysis area.

- Secondary ion images of $^{1}H^{16}O$ (in case of Cl), and ^{1}H and ^{13}C (in case of H) were monitored in real time during pre-sputtering to ensure that the area to be analyzed was free of cracks or hotspots indicative of contamination.
- Each analysis consisted of ~10 mins cycles for Cl and ~20 mins cycles for H, corresponding to a total analysis time of about 9 min and 18 min, respectively.

3. Results

The Cl isotopic composition and Cl content were obtained from 10 merrillite grains (17 analyses). The reported $\delta^{37}Cl$ is expressed as $\delta^{37}Cl = [(^{37}Cl/^{35}Cl)_{sample}/(^{37}Cl/^{35}Cl)_{standard} - 1]*1000$, relative to Standard Mean Ocean Chloride with a defined value of 0.0 ‰. The measured $\delta^{37}Cl$ ranges from -10.7 to 7.3 ‰, although subject to large uncertainties (3.4 to 6.6 ‰) as a result of the poor counting statistics because of the very low Cl content, while the Cl content ranged from 5 to 32 ppm.

The hydrogen isotopic composition (expressed as δD) and the H_2O content have been obtained from 4 merrillite grains (5 analyses overall) that were previously analysed for their Cl isotopic ratios and content. The analysed areas suggest a large variation in δD from 721 ± 35 ‰ up to 3496 ± 31 ‰, while the H_2O content ranged from 962 to 2341 ppm; these ratios display negative correlation to each other.

4. Conclusions

Our preliminary data indicate that Tissint`s merrillite may accommodates up to 32 ppm of chlorine, potentially representing the upper limit of Cl that can be accommodated in this nominally Cl-free phosphate. Furthermore, the low H_2O content [6] confirms minimal or no contamination from terrestrial environment or during samples preparation. The δD range may associated with variable level of modification which in turn is possibly related to interaction of Tissint with surficial processes on Mars (interaction with crustal fluids or the martian atmosphere) or influence of magmatic degassing. However, additional data for H content and isotopes are needed to further evaluate the most possible scenario that gave rise to the measured volatile signatures of Tissint.

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