A WATER-RICH PROTO-PLANET INFERRED BY TRIDYMITE AND PYROXENE IN THE OLDEST IGNEOUS ACHONDRITE NORTHWEST AFRICA 11119. A. Černok[1,2], K. Tait[1,2], M. Anand[3,4], I. R. Nicklin[1] L. White[1,2], T. Kizovski[1,2], X. Zhao[3], and I. A. Franchi[3]. [1]Centre for Applied Planetary Mineralogy, Department of Natural History, Royal Ontario Museum, Toronto, Canada, M5S 2C6 (acernok@rom.on.ca), [2]Department of Earth Sciences, University of Toronto, Toronto, Canada, M5S 3B1, [3]School of Physical Sciences, The Open University, Milton Keynes, MK7 6AA, UK, [4]Department of Earth Sciences, Natural History Museum, London, SW7 5BD, UK.

Introduction: The meteorite Northwest Africa (NWA) 11119 has been reported to be the oldest sample from a differentiated proto-planet, suggesting that volcanic activity on its parent body occurred 4563.3 ± 2.9 million years ago [1, 2]. It is a chemically evolved extrusive volcanic rock that has a silica-rich (andesite-dacite) bulk composition, with the highest modal abundance (~30 vol.%) of free silica of any known achondrite [1]. Intrigued by the fact that silicic volcanism on differentiated planets such as the Earth or Mars is promoted by abundant water dissolved in parental magmas, we investigated the water abundance and hydrogen isotope compositions of the phenocrysts in NWA 11119. Understanding the water budget and isotopic composition of rare ancient achondrite samples like NWA 11119 can lend insight into important questions relating to the source(s) of water in the earliest stages of inner solar system formation.

Methods: Hydrogen abundance and D/H ratios in tridymite and pyroxene phenocrysts were measured using CAMECA 50L nanoscale Secondary Ion Mass Spectrometer (NanoSIMS) located at the Open University. Following reported protocols [3], H abundances were calibrated using the measured $^{1}H/^{18}O$ ratios and the known H abundances of terrestrial basaltic standards (DR15, DR20 and DR32), that are pressed and polished within an indium mount. The abundance of the background water (≤ 20 ppm) and its isotopic composition was monitored and corrected using values obtained from San Carlos olivine. Single crystals of tridymite and pyroxene were handpicked from the sample and embedded in an indium mount to minimize the contamination by background volatiles. The silica polymorph tridymite was confirmed by Raman Spectroscopy at The Royal Ontario Museum.

Results: *Water abundance.* We find that tridymite has up to 244 ± 3 ppm H_2O, significantly more than orthopyroxene (Opx; or LPx for low-Ca pyroxene) and clinopyroxene (Cpx; or HPx for high-Ca pyroxene) that have up to 71 ppm H_2O (Fig. 1). The tridymite in NWA 11119 mostly resembles the Raman spectrum of a triclinic form (Fig. 2). The water content in the pyroxenes is comparable to that of the driest terrestrial pyroxenes [4], pyroxenes in Vesta-originated HED meteorites [5] and martian meteorites [6], but significantly drier than that those reported from primitive planetary objects such as grains from asteroid Itokawa and ordinary chondrites [7]. The partition coefficient between phenocrysts of Cpx (or HPx) and the surrounding melt that the crystals grew in equilibrium with, $D_{H2O}^{Cpx/Melt}$, was estimated at 0.011 ± 0.003 using the experimentally obtained calibration for basaltic magma composition of variable Al content, which is reported to be insensitive to pressure and temperature [8], and using the range of Al content in Cpx reported for this meteorite [1]. Using this $D_{H2O}^{Cpx/Melt}$, we estimated that the parental magma of NWA 11119 contained at least 2650 ppm H_2O (3885 ± 1231 ppm). This should be viewed as the lower limit because no corrections have been applied to take into account any diffusive loss of water from the crystals or the magma during its ascent and eruption at the surface. The estimated range of water content is comparable to that of many basaltic parental magmas on Earth.

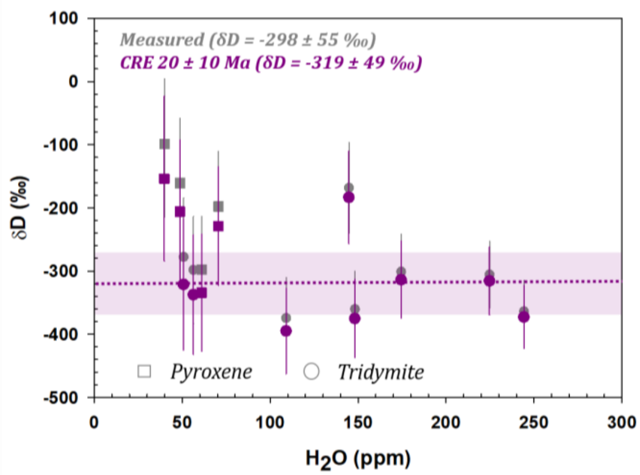

Figure 1. *H_2O-δD diagram of pyroxene and tridymite in NWA11119 meteorite. Grey symbols represent background corrected, purple symbols spallation corrected δD values (after Merlivat et al. 1976).*

H-isotopic composition can help discriminate between different reservoirs of water in the early solar system, with the two extremes being a D-poor protosun with the abundant H_2 in the surrounding protoplanetary disc (δD ~ -900 ‰), and the D-rich pre-solar ices (δD ~ 9000-13000 ‰). Determination of reliable D/H ratios and of associated uncertainties is dictated by H and D counting statistics, as reflected by the water contents of target phases. In the case of NWA 11119, tridymite contains significantly more water than pyroxene, and thus D/H ratios determined from tridymite are far more precise (Fig. 1). Background corrected δD in tridymite has a weighted average of -318 ± 48 ‰ (2σ, n=8) and does not significantly vary as a function of water abundances (Fig. 1), strongly implying that the crystals grew in a closed environment where no H isotopic fractionation took place (e.g. in a closed magmatic system). Pyroxenes, on the other hand, show slightly less negative average δD values of -205 ± 86 ‰ (2σ, n=4) although there is a significant overlap between the D/H ratios of tridymite and pyroxenes once the associated uncertainties are taken into account. The weighted average of δD values for all 12 measurements in silica and pyroxene is -298 ± 55 ‰ (2σ).

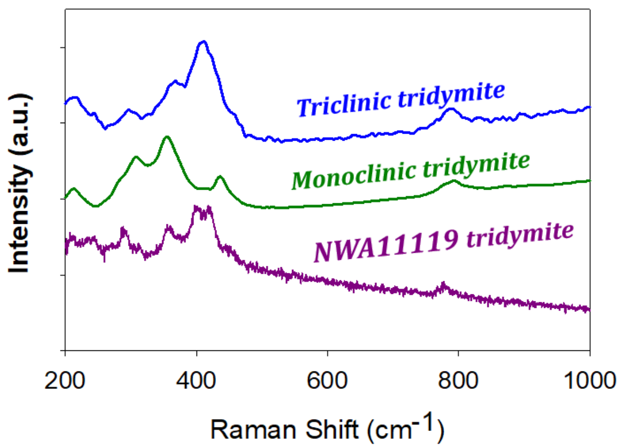

Figure 2. *Raman spectrum of tridymite in NWA 11119 compared to a monoclinic tridymite form (RRUFF R090042) and a triclinic form (RRUFF R040143).*

In meteorites, H and D can be added by cosmogenic sources during the time they spend travelling in space before arriving on Earth. As such, corrections for these contributions need to be applied to any measured H and D values. The cosmic exposure age (CRE) of NWA 11119 has not been yet reported, thus we calculate the spallogenic contribution of H and D assuming the most common CRE exposure reported for achondritic meteorites (20 ± 10 Ma). The range of CRE ages considered here are either longer or match that of achondrites that are chemically or chronologically comparable to NWA 11119 [1,2] including urelites, trachyandesitic fragment ALM-A from Almahata Sitta, and ungrouped achondrites NWA 7325 and Asuka 88139. As demonstrated in Fig. 1, the effect of spallogenic correction (using D-production rate after [9]) is negligible. A weighted average of δD over all 12 measurements corrected for 20 ± 10 Ma is -319 ± 49 ‰ (2σ), indistinguishable from the uncorrected ratio.

Discussion: The H-isotopic composition of water-bearing silica and pyroxene in NWA 11119 is well within the range of terrestrial mantle, lunar interior, 4 Vesta, the angrite parent body and possibly the martian interior [10]. Along with C- and S-type asteroids, these differentiated objects cover a relatively narrow range in H-isotopic composition (approx. δD −100‰ to −590 ‰) broadly matching that of the carbonaceous chondrites. The fact that crustal formation of NWA 11119 is dated at ~1-7 Ma after Ca-Al Inclusions (CAIs), possibly predating formation of carbonaceous chondrites (CCs) (~3-4 Ma after CAIs), suggests that a source of water comparable to that of CCs was available in the earliest stages of the solar system.

Conclusions: We have measured up to ~70 ppm of water (H_2O) in pyroxene and up to ~250 ppm in tridymite, the two main constituents of NWA 11119. Pyroxene data indicates at least ~2650 ppm of water in the parental melt, comparable to that of many basaltic parental magmas on Earth. This strongly suggests that NWA 11119 originated from a planetesimal that existed at the dawn of the solar system that was already producing water-rich magmas, similar to those on a differentiated, geologically evolved and habitable planet such as the Earth. Furthermore, the H-isotopic composition of the water implies that water-carrying planetesimals in the early solar system were similar to that of carbonaceous chondrites. This study proves that tridymite can hold significant quantities of water. As tridymite occurs pervasively in a range of planetary materials, its utility as a potential recorder of the history of water in the solar system is currently highly under-explored.

Acknowledgments: Louise Hawley Stone Charitable Trust supported obtaining a piece of the NWA 11119 meteorite. AC, LW, TK, and KT acknowledge the Hatch Ltd. Funding. MA and IAF acknowledge funding from the UK STFC (#ST/ P000657/1).

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