

# ATOM PROBE TOMOGRAPHY OF A 4.45 GA ZIRCON SUPPORTING EARLY CRYSTALLIZATION OF THE LUNAR MAGMA OCEAN. B. Zhang<sup>1</sup>, J. Greer<sup>2,3</sup>, D. Isheim<sup>4</sup>, D. N. Seidman<sup>4</sup>, A. Bouvier<sup>5</sup>, P. R. Heck<sup>2,3</sup>

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**Introduction:** The Moon was formed from an impact, i.e., the Giant Impact, between the proto-Earth and a Mars-sized impactor [1]. The newly-formed Moon was a largely molten sphere, a stage known as the lunar magma ocean (LMO) [2]. The LMO followed a differentiation sequence of mafic mantle + anorthositic crust → ilmenite-bearing cumulates → KREEP-rich melt (KREEP = potassium, rare earth elements and phosphorus) [2]. After the LMO crystallization, some mafic mantle cumulates transposed with the underlying denser ilmenite-bearing cumulates and intruded into the anorthositic crust to form the Mg-suite parental magmas [3]. This process is called the mantle overturn.

The timing of LMO crystallization is still debated. The formation of the Moon at 4510 Ma is constrained by the Hf model age of zircons [4], and the majority of LMO solidified  $\geq 4416$  Ma according to the oldest zircon  $^{207}\text{Pb}/^{206}\text{Pb}$  age thus far [5]. On the other hand, the Giant Impact could take place at  $\sim 4420$  Ma [6]. The  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  model age of mare basalts at 4353 Ma [7] and zircon ages peaking at  $\sim 4350$  [8] could mark the very late stage of LMO crystallization.

The formation of lunar zircons is related to the residual KREEP-rich melt of LMO, and thus their ages are suitable for constraining the very late stage of LMO crystallization [5]. Ages of zircons in the Mg-suite rocks likely place a lower limit on the LMO crystallization. A recent study shows that six oldest zircons found in an Apollo Mg-suite norite (named Civet Cat) have a concordant U-Pb age of  $4453 \pm 34$  Ma by ion-probe dating [9]. This could be the oldest lunar zircon age and may have important constraints on the timing of Giant Impact, LMO crystallization, and Mg-suite magmatism.

To test if this ancient zircon age is a result of unsupported radiogenic Pb clusters [10] or remaining Pb-retaining domains during normal Pb loss [11], we used atom probe tomography (ATP) to map the Pb distribution of zircon Z14 from the Civet Cat norite, which shows a  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $4453 \pm 47$  Ma [9].

**Methods:** Subsections of the zircon were milled to produce the nanotips. The tips were made using a focused ion beam (FIB) that milled away the top material. We used a Cameca LEAP 5000 XSi equipped with a picosecond UV laser, laser energy ranging from 50 to 200 pJ and repetition rate of 200 kHz. We analyzed three tips (A, B, and C) close to the 4399 Ma ion-probe pit and one tip (D) close to the 4453 Ma pit.

**Results:** The detected species include various H species, Y, HfO, Pb, and Th. The only isotope of Pb detected above the background is  $^{208}\text{Pb}^{++}$ , which is used as a proxy for all Pb isotopes. For this reason, we did not acquire the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios from the ATP analyses. All detected species in the four tips are homogeneously distributed on the nanoscale.

**Discussion:** The homogeneous distribution of Pb excludes the possible occurrence of unsupported Pb clustering in the zircon [9]. Our results indicate that the Pb mobilization found in the Civet Cat zircons [9] was most likely induced by normal Pb loss. The six oldest domains represent the Pb-retaining regions, and other younger domains result from various degrees of Pb loss induced by a shock event. As such, the concordant U-Pb age of  $4453 \pm 34$  Ma [9] is confirmed as the authentic crystallization age of Civet Cat norite zircons.

Our ancient zircon age places a lower limit for the LMO crystallization at  $\sim 4450$  Ma, and the Giant Impact should take place even earlier. The early LMO crystallization further implies that later anorthosite formation [12], mantle closure [7], and massive zircon formation [8] at 4350–4360 Ma might be a result of secondary magmatism after the LMO crystallization.

The crystallization age of Civet Cat norite zircons also indicates that the Mg-suite magmatism caused by the mantle overturn started as early as  $\sim 4450$  Ma, and the later Mg-suite magmatism at  $\sim 4330$  Ma [13] was likely induced by impacts [14].

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