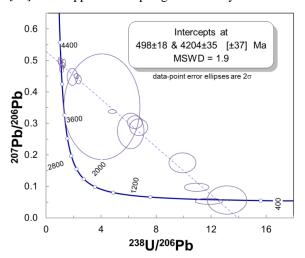
A YOUNG IMPACT EVENT RECORDED BY PHOSPHATES IN 78235 & 78236 NORITES. A. Černok<sup>1,2,3</sup>, M. Anand<sup>1,4</sup>, L. White<sup>2,3</sup>, J. Darling<sup>5</sup>, M. Whitehouse<sup>6</sup>, D. Fougerouse<sup>7</sup>, W. Rickard<sup>7</sup>, S. Reddy<sup>7</sup>, D. Saxey<sup>7</sup>, Z. Quadir<sup>7</sup>, K. Tait<sup>2,3</sup>, and I. Franchi<sup>1</sup>. <sup>1</sup>School of Physical Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom. <sup>2</sup>Centre for Applied Planetary Mineralogy, Department of Natural History, Royal Ontario Museum, Toronto, Canada, M5S 2C6. <sup>3</sup>Department of Earth Sciences, University of Toronto, Toronto, Canada, M5S 3B1. <sup>4</sup>Department of Earth Sciences, The Natural History Museum, London, SW7 5BD, United Kingdom. <sup>5</sup>University of Portsmouth, School of Earth & Environmental Sciences, Burnaby Road Portsmouth, PO1 3QL, United Kingdom. <sup>6</sup>Department of Geosciences, Swedish Museum of Natural History, Stockholm SE-104 05, Sweden. <sup>7</sup>School of Earth and Planetary Sciences, John de Laeter Centre, Curtin University, GPO Box U1987, Perth, WA 6845, Australia. (Email: acernok@rom.on.ca).

Introduction: The lunar norites collected as Apollo 17 samples 78235, 78236 and 78238 at station 8 in the Taurus-Lithrow Valley are igneous orthopyroxene-plagioclase cumulates with a strong KREEP signature [1]. Since the earliest petrographic descriptions, these norites were recognized as "the most heavily shocked" rocks in the Apollo collection [e.g. 2,3]. Shock effects include brecciation, mosaicism, undulatory extinction and shock lamellae in pyroxene along with transformation in plagioclase to diaplectic glass or melt, which implies peak shock-pressures in excess of 50 GPa and the overall extent of shock deformation of stage S5 and S6 [3, 4]. Importantly, all previous studies conclude that the texture of these rocks records only one major impact event [e.g. 2, 3]. Recent studies of whole rock and major mineral separates [5] found that the crystallization age of the shocked norite, based on Pb-Pb systematics, is  $4333 \pm 59$  Ma, which is concordant with a Sm-Nd age of  $4334 \pm 37$  Ma, and also a number of previous studies (summarized in [6]). However, significant disturbance in Rb-Sr isochron is explained by the heavy shock history of the rock [5]. A recent in situ Pb-Pb study of baddeleyite found a spread of relatively old ~4.2 – 4.3 Ga ages for which the authors proposed a scenario of a weak, second impact [7]. Recent Ar-Ar age of 4188  $\pm$ 13 Ma, concordant with earlier Ar-Ar studies [8 and refs. therein] ties very well with the abovementioned ages.

**Motivation:** Inspired by recent observations of disturbance of Pb-Pb and U-Pb systematics in various shock-affected accessory minerals [e.g. 9, 10], we determined *in situ* ages of phosphates in norites 78235 & 78236. The choice of samples is based on our previous electron backscatter diffraction (EBSD) study [4], where we observed high intra-grain crystal-plastic deformation (S5) and recrystallization (S6) in apatite and merrillite. Furthermore, to better understand the effects of shock-induced microstructure on the U-Pb system, we performed atom probe tomography (APT) and transmission electron microscopy (TEM) of one highly-shocked (S5) apatite grain.

**Methods:** U-Pb isotopic measurements were performed using a CAMECA 1280 ion microprobe at the NordSIMS facility, located at the Swedish Museum of Natural History (Stockholm), following previously reported protocols for Ca-phosphate analyses [e.g. 11]. Eight apatite and ten merrillite grains were analyzed in the two thin sections. APT and TEM work on the selected apatite grain in 78236 was performed at the JdLC in Curtin University, Perth. We analyzed eight APT tips from a single lift out and one TEM foil in this study.

**U-Pb ages of 78235 & 78236 phosphates:** Individual  $^{207}$ Pb/ $^{206}$ Pb SIMS ages range from 4236  $\pm$  29 (2 $\sigma$ ) Ma to much younger ages, implying substantial Pb loss in both apatite and merrillite. A Tera-Wasserburg diagram of these U-Pb analyses (Fig. 1) reveals that all analyzed grains fall on a discordia line with an upper intercept of 4204  $\pm$  35 Ma (2 $\sigma$ ) and a lower intercept of 498  $\pm$  18 Ma (2 $\sigma$ ). The upper intercept phosphate age is ~100 Ma younger than what was interpreted as crystallization Pb-Pb ages of baddeleyite in this sample [7] but also of baddeleyite in the unshocked troctolite 76535 [13]. The upper intercept age is broadly observed in



**Figure 1.** Tera-Wasserburg diagram of U-Pb isotopic composition in 18 phosphate grains from 78235 and 78236 norites. The upper and the lower intercept are annotated. Regression is not constrained through a fixed origin.

phosphates from the less shocked Mg-suite samples (76335 and 76533, ref. [12]) and it ties very well with the reported Ar-Ar age [8]. Thus we interpret it as the age when the norites cooled below the U-Pb closure temperature of apatite (~450 °C), most likely after the pervasive impact at ~4.25 Ga [7] that induced the S5-S6 deformation. The lower intercept indicates a substantial, and in some grains even complete, Pb-loss in apatite and merrillite at ~500 Ma. This disturbance of the U-Pb system has not been recorded in any other geochronometer applied to these rocks [summarized in 6]. It also differs significantly from the measured cosmic exposure age (CRE, ~260 Ma [8]). The Pb-loss was most likely caused by a thermal event that does not appear to have disturbed other isotopic systems.

Sub- $\mu$ m structure of shocked apatite: Stable throughout TEM analysis, shocked apatites show good overall crystallinity, appearing finely granular with crystallites ranging in size from ~nm to ~ $\mu$ m in scale. Changes in grey-scale contrast in bright field (BF) TEM images reveal variation in orientation as a result of deformation within larger crystallites (~ $1\mu$ m), whereas a sharp BF contrast of ~50 to 100 nm crystallites implies their severe deformation induced fragmentation, which is reflected in the rings in diffraction patterns (Fig. 2).

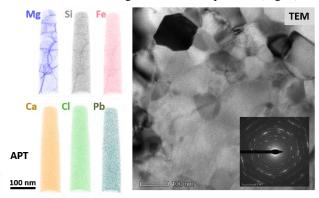


Figure 2. APT tips revealing distribution of major and trace elements in apatite (78236) at sub-µm scale. TEM BF image indicates the crystallite size. The inset show indexed diffraction pattern of the area.

The smaller crystallites form grain boundaries meeting at 120° triple junctions. This equilibrium texture is likely a result of thermal annealing of apatite exposed to post-shock heating from the surrounding melted plagioclase, caused by a major, primary impact. The atom probe lift outs were selected from the area dominated by smaller crystallites. The complex microstructure of the well-developed sub-grains with clear 120° grain boundaries are defined by segregation of Mg, Si and Fe impurities. Following a recent study [14], we attempted to isolate U-Pb and Pb-Pb ages from different subdomains

of the apatite tips. Unfortunately, <sup>238</sup>U, expected to occur as oxidized compounds at 270 and 135 Da, and <sup>206</sup>Pb<sup>++</sup> recorded at 103 Da (mass-to-charge ratio), respectively, were too low to quantify above background. Singly charged U and Pb were not observed. However, we were able to measure overall Pb abundance (<sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb) within the Mg-enriched features revealing lower Pb abundances than in the Mg-poor subgrains. This suggests Pb mobilization and loss along the boundaries between recrystallized subgrains. Although observed at nm-scale, Pb-mobilization can be considered grain-wide because it is present in all eight tips that are lifted out along a ~15 μm long profile.

**Discussion and conclusions:** The lower intercept age of 498 ± 18 Ma could not correspond to U-Pb resetting induced by a major impact event, responsible for the broad S5-S6 deformation of the norites, as such an event would have caused partial to complete resetting of all other geochronometers. Instead, a minor thermal event must have reactivated the existing nm-scale grain boundaries, present in the recrystallized phosphates, to allow for Pb-loss at 498 ± 18 Ma. If a minor impact is responsible for the Pb loss at ~500 Ma, then an older, larger impact is responsible for the high-grade (S5-S6) whole rock deformation and sub-grain annealing of the apatite. A recent hypothesis of an impact at ~4.25 Ga [7], very soon after the crystallization, fits well with this scenario. Based on our current understanding of the thermal evolution of the lunar interior, it is unlikely that the heating at ~500 Ma was caused by volcanism or a similar indigenous process. Interestingly, this age is concordant with the lower intercept of the apatite U-Pb systematics in Novato L6 ordinary chondrite  $(473 \pm 38 \text{ Ma}, [15])$ , interpreted to reflect a major disturbance related to the catastrophic disruption of the L chondrite parent body [16].

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