POWDER X-RAY DIFFRACTOMETRY OF THE ORGUEIL CARBONACEOUS CHONDRITE: INSIGHTS INTO THE CLAY MINERALOGY Laurence A.J. Garvie[1,2], [1]Center for Meteorite Studies, [2]School of Earth and Space Exploration, Arizona State University, 781 East Terrace Rd., Tempe, AZ 85287-6004 (lgarvie@asu.edu).

Introduction: The Orgueil carbonaceous chondrite has received considerable scientific attention since its fall in 1864 [1], in part because of its cosmic composition and hydrous clay-rich nature. The identity of the clay has proven difficult in part because of its fine-grained nature and broad, relatively indistinct reflections. The dominant ~7 and 14 Å reflections have been ascribed to a range of phyllosilicates. However, the reflections are most consistent with serpentine and smectite [2]. TEM studies show compositional data and d-spacings consistent with Fe-bearing, Mg-rich serpentine and saponite [3]. In addition, the HRTEM images suggest a certain degree of interstratification of serpentine and saponite. Quantitative powder XRD show that Orgueil is ~83 vol% serpentine/saponite [4]. Here, further insights into the bulk nature of the clays are provided by powder x-ray diffraction (XRD) of samples prepared using 'standard" clay identification procedures.

Samples and preparation: Powder XRD patterns were acquired with a Rigaku MiniFlex 600 diffractometer, with a post-diffraction monochromator, and Cu Kα radiation. Data were acquired from whole rock and separated clays fractions. Clay fractions were prepared by crushing ~0.5 g of Orgueil in water and using a centrifuge to separate the 2 to 0.5, and <0.5-μm clay fractions. These fractions were then divided into two portions and exchanged with 0.1M $CaCl_2$ and 1M KCl solutions, respectively. These clays were then mixed with a few ml of water and deposited onto glass slides forming oriented clay mounts. XRD patterns were acquired under a range of humidities, after saturation with ethylene glycol (60 °C, 24 hrs), and after heating at 300 ° and 500 °C for 1 hour.

Results and discussion: The bulk powder XRD profiles show sharp, intense reflections for magnetite, and less intense sharp peaks for dolomite, pyrrhotite, and possibly olivine. These peaks sit on a series of broad reflections from clays, prominently observed by the broad low-angle peaks near 15.5 and 7.5 Å, and two prism-like structures starting near 20 ° and 25 °2θ. The overall pattern is similar to that acquired by synchrotron XRD [Nozaki], with minor differences in the intensities of the sharp reflections.

The air-dried, Ca-saturated, <0.5 μm clay fraction of randomly oriented and oriented samples show intense but broad reflections centered near 15.5 and 7.5 Å, and a prism-structure near 25 °2θ (Fig. A,B). After K-saturation the 15.5 Å reflection is broader and shifts to 12.8 Å. The randomly oriented pattern from the air-dried Ca-saturated clay is dominated by 00*l* reflections for smectite and serpentine and two-dimensional *hk* diffraction bands from smectite (Fig. A). The smectite prism is absent in the patterns from the oriented clay samples, though the serpentine prism is prominent.

Etylene-glycol solvation shifts the 001 peak from the Ca-saturated smectite to 18.06 Å (Fig. B), with a new peak at 8.34 Å. The K-saturated clay (not shown) has a broad, poorly resolved peak at 19.7 Å and less intense reflection at 8.39 Å. After heating the Ca-saturated clay to 300 ° and 500 °C, the 001 reflection collapses to 9.76 and 9.32 Å, respectively. For all of the treatments, a comparatively weak intensity 001 serpentine peak remains unshifted at 7.46 Å.

Ferrihydrite has been identified by electron diffraction in Orgueil [3] and said to be "very abundant", with reflections at ~2.58 and 1.50 Å. However, these reflections overlap with the smectite *hk* diffraction bands: hence ferrihydrite cannot be definitively identified in the clay patterns, though suffice it to say that it does not contribute significant intensity to the patterns.

The d-spacings and behavior of the reflections after the treatments are broadly consistent with a mixture of serpentine and smectite, consistent with previous analyses [2]. However, the serpentine 001 spacing of 7.46 Å is significantly larger than that observed in other serpentines, which are typically 7.2 to 7.3 Å. The d-spacing of the 06, 33 *kh*/060 reflection match that for trioctahedral clays. Ethylene-glycol-solvated smectites typically yield a basal spacing near ~17 Å, with a rational series of higher-order reflections. In contrast, the Orgueil clay swells to ~18.06 to 19.7 Å.

The patterns are consistent with clays that are fine-grained and exhibit a high degree of disorder. While TEM has revealed well-crystallized grains, the XRD patterns indicate that disordered clays predominate. The broadness of the smectite peaks is a result of a combination of interstratification, intercalation, and small grain size. Intercalation, such as from silica [6] or carbon [7], affects the swelling properties and could partly account for the broadness of the reflections after heating. The non-integer 00l versus 002 spacing could indicate a degree of random interstratification. The relatively high 001 d-spacing for the serpentine is likely the result of small diffracting domains with, on average, few ~N<10 layers per crystallite.

A question the XRD data raises is why aren't the clays better crystallized? As reviewed in [1], alteration occurred between 0° and 150° C, and assuming the clay formation coincided with the crystallization of the dolomite and breunnerites, then formation occurred over ~7 to 9 Myrs time period. The poorly crystalline nature of the clays suggest they formed rapidly and did not undergo significant recrystallization by Ostwald ripening.

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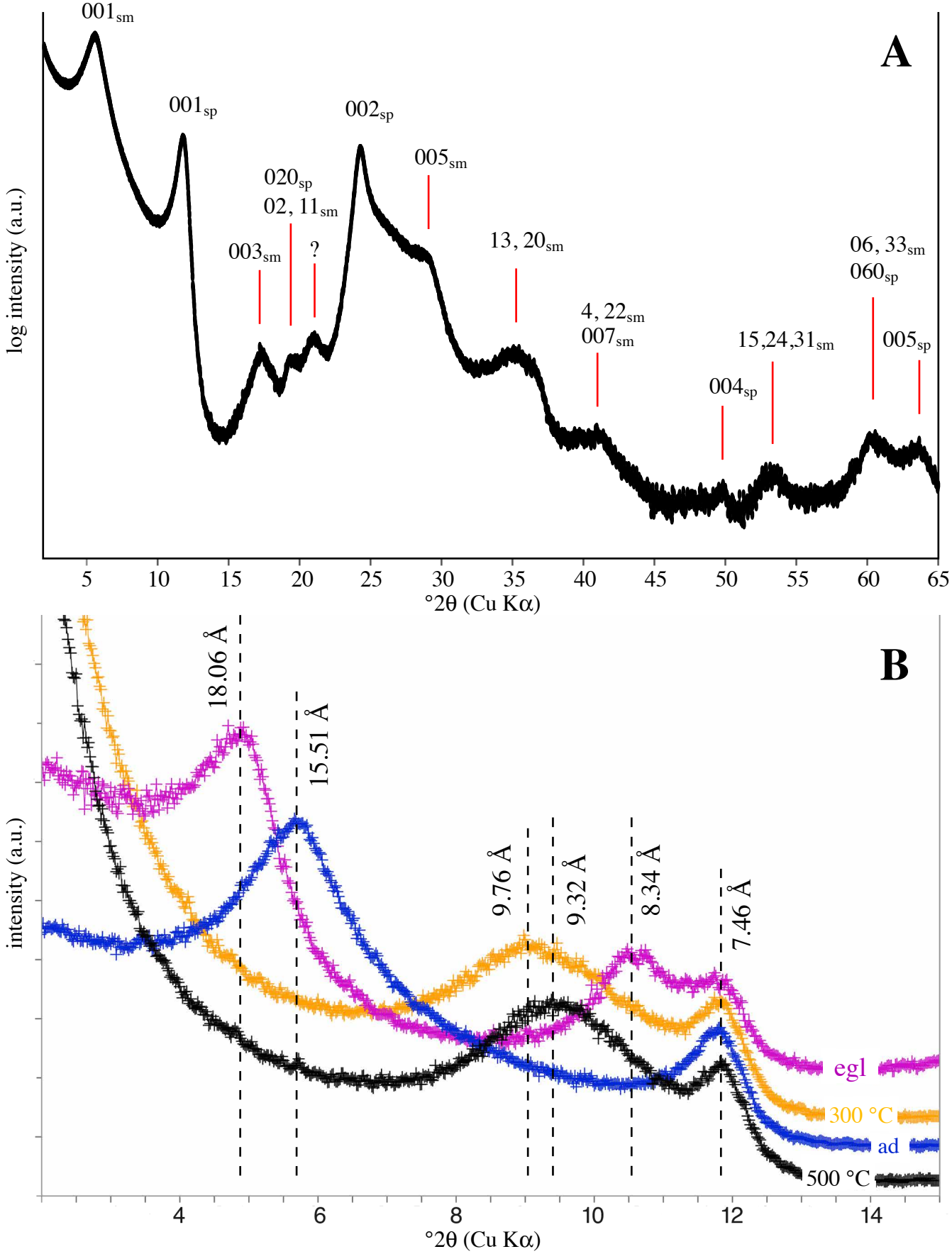
References: [1] Gounelle and Zolensky (2014) MAPS, 49, 1769-1794. [2] Bass (1971) GCA, 35, 139-147. [3] Tomeoka and Buseck (1988) GCA, 52, 1627-1640. [4] King et al. (2015) GCA, 165, 148-160. [5] Nozaki et al. (2006) MAPS, 41, 1095-1114. [5] Endo et al. (1980) Clays Clay Miner, 28, 105-110. [6] Garvie and Buseck (2007) MAPS, 42, 2111-2117.



Powder X-ray diffraction (XRD) data from the <0.5 µm Ca-saturated Orgueil clay fraction. A) Pattern from a randomly oriented mount under air-dried conditions. sm - smectite, sp - serpentine. B) Patterns from oriented mounts acquired under the air dried (ad), ethylene glycol saturated (egl), and heated to 300 and 500 °C conditions. Profiles arbitrarily shifted along the y-axis for clarity.