

APPLICATION OF AN ALKYLAMMONIUM METHOD FOR CHARACTERIZATION OF PHYLLOSILICATES IN CI CHONDRITES: D. C. Golden¹, D. W. Ming², M. E. Zolensky², and S. V. Yang³; ¹Dual Inc., ²NASA-JSC, ³Lockheed ESC, Houston, TX 77058

INTRODUCTION. Many meteorites and interplanetary dust particles (IDPs) with primitive compositions contain significant amounts of phyllosilicates, which are generally interpreted as evidence of protoplanetary aqueous alteration at an early period in the solar system [1]. These meteorites are chondrites of the carbonaceous and ordinary varieties. Characterization of phyllosilicates in these materials is important because of the important physico-chemical information they hold, e.g., from well characterized phyllosilicates, thermodynamic stability relations and hence the conditions of formation of phyllosilicates in the parent body of the meteorite can be predicted. Although we are at a rudimentary level of understanding of the minerals resulting from the aqueous alteration in the early solar nebula, we know that the most common phyllosilicates present in chondritic extraterrestrial materials are serpentines, smectites, chlorites and micas [2]. The characterization of fine grained minerals in meteorites and IDPs rely heavily on electron beam instruments, especially transmission electron microscopy (TEM). Typically, phyllosilicates are identified by a combination of high resolution imaging of basal spacings, electron diffraction analysis, and chemical analysis. Smectites can be difficult to differentiate from micas because the smectites lose their interlayer water and the interlayers collapse to the same basal spacing as mica in the high vacuum of the TEM. In high-resolution TEM (HRTEM) images, smectite basal spacings vary from 1 nm (fully collapsed) up to 1.5 nm, while micas show 1 or 2 nm basal spacings. Not only is it difficult to differentiate smectites from micas, but there is no way of identifying different classes of smectites (e.g., low-charged smectite, high-charged smectite, vermiculite, etc.) in meteorites and IDPs. To differentiate smectites from micas and also to recognize the charge differences among smectites, an alkylammonium method can be employed because the basal spacings of alkylammonium saturated smectites expand as a function of alkylamine chain length and the layer-charge density of the 2:1 expanding phyllosilicate, and the final product is significantly more stable under electron beam examination. Such a method was tested on standard clays and several meteorite samples using four alkylammonium salts ($N_c = 9, 12, 14$ and 18) [3]. This test clearly established the usefulness of alkylammonium technique in stabilizing the phyllosilicates under the electron beam and in expanding the layers to illustrate layer charge. However the alkylammonium saturation was carried out by equilibrating the sample thin sections with alkylammonium solutions for only 5 to 10 min. in the previous study. This equilibration time appeared to be too short to cause complete expansion. The current study was carried out to achieve complete saturation of the phyllosilicates by alkylammonium ions. A longer equilibration time of up to 4 hr was employed on thin sections of three meteorites and two standard clays. Alkylammonium solutions of a full range of N_c values from 6 to 18 were used to achieve complete expansion of the layers and hence permit complete characterization of the smectites with respect to layer charge density. The procedure presented discriminates the smectites from other minerals and allows the estimation of the smectite layer charge. The method therefore is suitable for studying the charge bearing phyllosilicates in meteorites and should be applicable to IDPs which cannot be examined by traditional mineralogical methods due to their sample size limitations ($< 100 \mu\text{m}$).

MATERIALS AND METHODS. Three CI chondrites (Alais, Ivuna, and CI clasts from Kaidun) and two standard clays (saponite from Ballarat, California and nontronite from Garfield, Washington) were embedded in Embed 812 epoxy and cut into 50-70 nm thin sections. The sections were placed on a C-coated holey plastic substrate mounted on Cu grids. Grid-

PHYLLOSILICATES IN CI CHONDRITES; Golden et al.

containing sections were dried and then transferred into an alkylammonium solution of predetermined concentration in a one-ml Eppendorf tube placed in an incubator set at 65°C. Samples were gently shaken for 30 sec at hourly intervals for 4 hr. At the end of 4-hr period the Eppendorf tube and the contents were quickly transferred into a beaker containing warm (65 °C) deionized water. The grid was picked up with tweezers and then repeatedly washed in warm deionized water three additional times and dried.

RESULTS AND DISCUSSION. HRTEM images were used to measure the layer spacings of the alkylammonium-treated standard phyllosilicates and meteorite samples. The phyllosilicate standards expanded to characteristic d-spacings depending upon the chain length of the alkylammonium ion and the interlayer charge density of the individual standard. For example, the saponite saturated with $N_c = 8$ alkylammonium ions had predominantly 1.3 nm spacing (monolayer) and as the N_c value was increased to 16, 1.75 nm spacings (bilayer) appeared more frequently. At $N_c > 16$ only 1.75 nm and higher d-spacings were visible. Similar changes were observed for nontronite, however, the monolayer to bilayer transition appeared at shorter chain lengths suggesting a higher average layer charge for nontronite than saponite. In the meteorite samples serpentine spacings were unaffected by the alkylammonium treatment (0.7 nm). Smectites in the meteorites expand to layer d-spacings according to the alkyl chain length and their layer charge. Typically, these d-spacings ranged from 1.35 to about 2.3 nm. A spacing of 1.35 nm corresponds to monolayer occupation of alkylammonium ions and 1.75 nm corresponds to bilayer occupation [4]. The presence of different spacings for a single alkylammonium ion saturated phyllosilicate in meteorites indicated charge heterogeneity among layers similar to that observed in terrestrial phyllosilicates [4].

The matrix of the Alais meteorite consisted mostly of phyllosilicates. It had uniformly stacked, slightly bent nanocrystals of smectite (saponite), consisting of 5 to 30 2:1 layers and ranged from 50 to 500 nm in diameter. Thin packets of serpentine layers (2 to 3 layers thick) appeared to be sparsely embedded in larger smectite crystals in concurrence with earlier observations [5,6], suggesting a genetic relationship between serpentine and smectite. The Ivuna meteorite contained predominantly smectite crystals, similar to those of Alais; the serpentine crystals observed here were larger (15 to 20 layers thick) than those observed in Alais. The Kaidun meteorite had fewer phyllosilicates in comparison to the other two. Phyllosilicate thickness here ranged from 2 to 15 layers and the diameter of the platy crystals ranged from 25 to 75 nm. An occasional 1 nm d-spacing was observed suggesting the presence of a mica. Otherwise the phyllosilicates were mostly smectites and serpentines. In addition to smectites, Kaidun contained pentlandite and pyrrhotite in agreement with earlier observations [5,7]. From the expansion of the phyllosilicates in the meteorite by alkylammonium ions, charge density variations in the smectites could be inferred. Ivuna and Kaidun matrices contained smectite nanocrystals of approximately similar low charge (<0.4 eq/ $(\text{Si,Al})_4\text{O}_{10}$). Alais contained well-defined crystals of smectite with slightly higher charge and exhibited greater layer charge homogeneity. The layer charge heterogeneity of the former two samples, Ivuna and Kaidun, suggests complex reactions during the parent body aqueous alteration (hydrothermal?) process [8].

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