CALC-SILICATE METASOMATISM IN CM CHONDRITES SHIDIAN AND KOLANG: THE FIRST REPORT OF ASTEROIDAL HYDROANDRADITE. L. E. Jenkins[1], M. R. Lee[1], L. Daly[1,2,3], A. J. King[4], and S. Li[5]. [1]School of Geographical and Earth Sciences, University of Glasgow, Glasgow, Scotland (l.jenkins.1@research.gla.ac.uk) [2]Australian Centre for Microscopy and Microanalysis, The University of Sydney, NSW, 2006, Australia, [3]Department of Materials, University of Oxford, Oxford, OX1 3PH, UK , [4]Planetary Materials Group, Natural History Museum, London, England. [5]Lunar and Planetary Science Research Center, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China

Introduction: It is important to understand water-rock reactions recorded by meteorites as they have implications regarding volatile sources within our solar system and the formation of planetesimals. Carbonaceous chondrites have undergone aqueous alteration and have abundant secondary hydrous phases. The petrology of these secondary phases can inform our understanding of the environmental conditions of water-rock reactions. We studied secondary minerals within the Mighei-like carbonaceous (CM) chondrites, Shidian and Kolang, focusing on a hydrous Ca-Fe silicate that has not yet been described in meteorites.

Methods: A polished rock slice of Shidian ~126 mm^2 in area and two thin sections of Kolang, both ~2 cm^2 in area, were studied. They are recent falls (2017 and 2020, respectively) and both have a petrologic subtype of 2.2 [1,2].

To evaluate their petrography, montaged back-scattered electron (BSE) images and energy dispersive X-ray spectroscopy (EDS) maps were collected using a Carl Zeiss Sigma variable pressure analytical scanning electron microscope (SEM) at the Imaging Spectroscopy and Analysis Centre (University of Glasgow, UoG). Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were obtained from focused ion beam sections using a FEI T20 TEM in the Kelvin Nanocharacterisation Centre, UoG. The chemical compositions of the Ca-Fe silicate was determined by wavelength dispersive X-ray spectroscopy using a CAMECA SX100 electron probe microanalyzer (EPMA) at the University of Edinburgh.

Results: BSE and EDS maps of both meteorites revealed a peculiar Ca- and Fe-rich silicate phase (Fig. 1). The only mineral matching this phase's chemical composition is hydroandradite ($Ca_3Fe^{+3}_2(SiO_4)_{3-x}(OH)_{4x}$). Hydroandradite was observed in four different morphologies (Fig. 1): 1) associated with sulphides in layered globules, 2) associated with perovskite, 3) in small (~5 µm) spheroids resembling magnetite spheroids, and 4) layered with magnetite, pentlandite, and apatite. Kolang contains hydroandradite occurring in all four morphologies, whereas Shidian only has the sulphide-associated hydroandradite.

TEM images of perovskite associated hydroandradite in Kolang show it as a monomineralic finely polycrystalline phase. SAED patterns are consistent with cubic symmetry with unit-cell parameters of a≈12.3 Å.

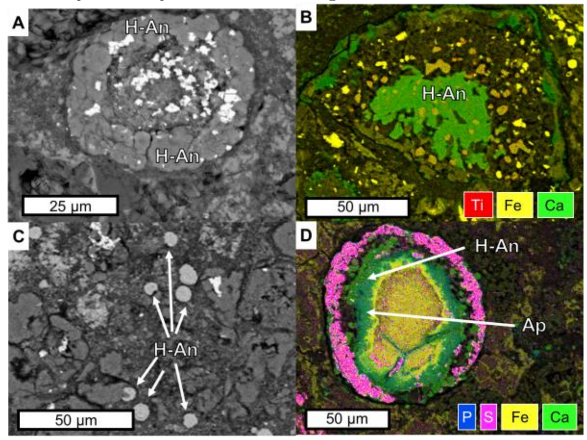

Fig. 1. Hydroandradite (H-An) morphologies. A) BSE image of sulphide-associated H-An in Shidian. Sulphides are white while H-An is grey. B) Ti-Fe-Ca EDS map of perovskite-associated H-An in Kolang. H-An is olive green, perovskite is brown-orange, and magnetite is yellow. C) BSE image of H-An spheroids in Kolang. D) P-S-Fe-Ca EDS map of layered H-An (olive green, magnetite (yellow), pentlandite (pink), and apatite (Ap) (turquoise) in Kolang.

EPMA data from four analyses of hydroandradites in Shidian gave an average total of 84.7±2.0 wt. % (Table 1). The average composition of hydroandradite in Shidian is $Ca_{3.0}(Fe_{1.5}Mg_{0.4}Ti_{0.1}Al_{0.1})(SiO_4)_{2.4}(OH)_{2.4}$, calculated on the assumption that Ca exclusively occupies the *X* site with the proportions of OH^- calculated based on amount of Si, as in hydroandradite, OH^- replaces SiO_4 (Table 1).

Table 1. Chemical composition of hydroandradite.

	Shidian (n=4)	Kolang (n=12)
Ca (wt%±σ)	20.6±1.5	23.5±2.4
Fe^{3+} (wt%±σ)	19.4±1.7	18.4±1.5
Si (wt%±σ)	10.7±0.3	10.2±0.7
Mg (wt%±σ)	2.1±0.1	0.4±0.6
Ti (wt%±σ)	0.4±0.1	1.7±0.8
Al (wt%±σ)	0.7±0.1	0.5±0.3
O (wt%±σ)	28.8±0.6	28.7±1.2
Total (wt%±σ)	84.7±2.0	83.7±1.8

EPMA data for 12 analyses of perovskite-associated hydroandradites in Kolang have similar totals of 83.7±1.8 wt. % (Table 1), and an average composition of $Ca_{3.0}(Fe_{1.1}Mg_{0.1}Ti_{0.3})(SiO_4)_{2.0}(OH)_{3.9}$.

Discussion: *Identification of Hydroandradite.* The SAED patterns are consistent with the unit-cell parameters of hydroandradite [3,4]. Given the low totals from the EPMA data, this phase is assumed to have an unanalyzed component. This component is likely OH^- that is substituting for Si because there is only ~10 wt% Si present, much lower than what is needed for anhydrous andradite (~15 wt% of Si).

Formation of Hydroandradite in CMs: On Earth, hydroandradite is formed during low temperature (150-300°C) calc-silicate metasomatism by Ca-rich and Si-poor fluids, where it replaces other phases [5]. In contrast, most estimates are that CM chondrite alteration took place at <130°C [6]. However, this is not the first occurrence of secondary minerals that formed above typical aqueous alteration temperatures in CMs. Lee et al. [6] described sodalite that formed above 100°C in the CM chondrite Meteorite Hills (MET) 01075 [6]. The presence of hydroandradite in Kolang and Shidian is further evidence for metasomatic alteration of the CM parent body(ies) occurring above 100°C.

Terrestrial hydroandradite has been recorded replacing ilmenite, perovskite, magnetite, and titanite [3,5]. Also, andradite (hydroandradite's anhydrous counterpart) has been reported in CV and CO carbonaceous chondrites, as well as in the complex CR chondrite breccia Kaidun [7,8]. In CV and CO chondrites, andradite is proposed to have replaced hedenbergite [7]. Hydroandradite is always replacing another mineral and it is therefore important to identify the precursor mineral assemblages.

The sulphide-associated hydroandradite occurs in layered roughly circular objects (Fig. 1a). These objects bear some resemblance to magnetite-sulphide rosettes in the CM-related carbonaceous chondrite Northwest Africa (NWA) 12563 [9] in that both are layered, roughly spherical structures. Hydroandradite may have replaced magnetite in these rosettes, leading to the layered hydroandradite-sulphide assemblages. Given that these magnetite-sulphide rosettes display replacement textures and require at least two generations of aqueous fluids to form [9], hydroandradite's replacement of magnetite indicates a minimum of three aqueous alteration events on the CM parent body.

The precursor assemblage to the perovskite-associated hydroandradite in Kolang is most likely a calcium-aluminum-rich inclusion (CAI). The hydroandradite is Ti-rich (Table 1) and Ti is usually not a fluid mobile element [5]; its presence in hydroandradite is likely due to its abundance in the precursor mineral. This hydroandradite occurs with perovskite ($CaTiO_3$). Because hydroandradite is known to replace perovskite on Earth [3], this hydroandradite likely formed by partial replacement of perovskite. It is also possible that hydroandradite replaced hibonite, a common Ti-bearing mineral in CAIs from CMs.

The third morphology of hydroandradite in Kolang is as small spheroids that resemble magnetite spheroids in other clasts within the same meteorite (Fig. 1c). Hydroandradite has therefore likely replaced some of the magnetite spheroids. Given that magnetite spheroids form during aqueous alteration [10], their replacement by hydroandradite is further evidence for multiple aqueous alteration stages.

The final morphology of hydroandradite occurs with magnetite, pentlandite, and apatite. These three minerals are known to form during alteration of kamacite with fluids that have low amounts of cations [11], similar to the fluids that form hydroandradite on Earth [5]. Unlike the other morphologies, this hydroandradite likely formed alongside the magnetite, apatite, and pentlandite in the same aqueous alteration event.

Conclusion: Hydroandradite was identified in the CM chondrites Kolang and Shidian, where it has replaced magnetite, perovskite and/or hibonite, and kamacite during metasomatism at >150°C. Magnetite in CM chondrites is a product of aqueous alteration, thus its replacement by hydroandradite indicates multiple stages of aqueous alteration that occurred under contrasting physiochemical conditions to allow different secondary phases to form.

Andradite has been previously reported in carbonaceous chondrites [7, 8], but this is the first report of asteroidal hydroandradite. The fact that it is observed in not one, but two CMs indicates either: 1) hydroandradite is likely present in other CMs but has not yet been identified; 2) Kolang and Shidian are from a distinct parent body that experienced hydroandradite-forming metasomatic events.

Acknowledgements: We thank Mendy Ouzillou for providing Kolang samples. We thank Peter Chung for collecting BSE and EDS maps and Chris Hayward for collecting the EPMA data used. We thank Billy Smith for preparing FIB samples for TEM and Colin How for assisting with TEM data collection.

References: [1] Fan Y. et al. (2020) 51st LPSC, Abstract #1234. [2] King A. J. et al. (2021) 52nd LPSC, Abstract #1909. [3] Schmitt A. C. et al. (2019) *J. Mineral. Petrol. Sci.* **114:** 111-119. [4] Armbuster T. (1995) *Eur. J. Mineral.* **7 :** 1221-1225. [5] Ghosh B. et al. (2017) *Chem. Geol.* **457:** 47-60. [6] Lee et al. (2019) *MAPS.* **54:** 3052-3063. [7] Ganino C. and Libourel G. (2020) *Sci. Adv.* **6:** eabb1166. [8] Zolensky et al. (1996) *MAPS.* **31:** 484-493. [9] Hewins R. H. et al. (2021) *Geochim. Cosmochim. Acta.* **311:** 238-273. [10] Bunch and Chang (1980) *Geochim. Cosmochim. Acta.* **44:** 1543-1577. [11] Palmer E.E. and Lauretta D.S. (2011) *MAPS.* **46:** 1587-1607.