FORMATION AND PRESERVATION OF METHANE IN AQUEOUSLY ALTERED AND SHOCKED CM CARBONACEOUS CHONDRITES. P. Lindgren[1], N.J.F. Blamey[2], J. Parnell[3] and M.R. Lee[1], [1]School of Geographical and Earth Sciences, University of Glasgow, Gregory Building, Lilybank Gardens, Glasgow G12 8QQ, UK, [2]Department of Earth Sciences, Brock University, 500 Glenridges Avenue, St Catharines, Ontario L2S 3A1, Canada, [3]School of Geosciences, Meston Building, Old Aberdeen AB24 3UE, UK, E-mail: paula.lindgren@glasgow.ac.uk

Introduction: Methane (CH_4) on Earth is widely produced by methanogens during the anoxic breakdown of biomass, but it can also form via non-biological processes e.g. serpentinisation involving the aqueous alteration of olivine in the presence of carbon dioxide [1]. Possible abiotically formed methane on Earth has been detected in contexts including fluids from hydrothermal vents in ultramafic rocks on the sea floor [2], hydrothermal mineral deposits and serpentinites from ophiolite suites [3], and within a wide range of basalts [4]. Most recently, methane was discovered within martian meteorites, also inferred to have formed through serpentinisation [5]. However, serpentinisation is not the only abiotic process that can produce methane. For example, previous studies have shown that carbonaceous micrometeorites could be carriers of methane to Mars's surface by generating the gas upon ablation (pyrolysis) during atmospheric entry [6]. Methane has also been found to be produced via experimental ultraviolet-radiation of CM, CR and CV carbonaceous chondrites [7,8]. A better understanding of abiotic methane formation is important since the detection of methane on remote planetary surfaces and atmospheres could be a false life detection signature.

Aim of study: In this study we have sought methane in a suite of CM carbonaceous chondrites that are serpentinised and shocked to various degrees. Here we ask (i) was methane generated during aqueous alteration and serpentinisation on the CM parent bodies? and (ii) is methane preserved within the CM meteorites after the ~4.56 billion years during which they have experienced multiple phases of deformation and shock [e.g. 9]? Ultimately, we ask if aqueously altered CM carbonaceous chondrites could be responsible for adding methane to planetary surfaces.

Aqueous alteration of CM chondrites: The CM chondrites are derived from primitive asteroids that were aqueosly altered ~4563+0.4/-0.5 Ma ago [10] when fluids released by the melting of H_2O- and CO_2-rich ices reacted with primary anhydrous phases including olivine. These reactions resulted in the formation of secondary minerals, primarily serpentine. CMs contain on average ~75 vol. % serpentine, more or less depending on their degree of aqueous alteration [11]. The scale of aqueous alteration of most CMs range from CM2.0 to ~2.6 [12], where CM2.0 refers to the highest degree of aqueous alteration, and CM2.6 is the lowest. The least altered CMs (i.e. >CM2.6) are extremely rare [13].

Methods: This study used whole rock chips weighing between 0.16 and 0.34 gram of four carbonaceous chondrites, of which one was the essentially unaltered CV3 Allende (for comparison), and the remaining three were CM2s ranging from the severely aqueously altered Scott Glacier (SCO) 06043 (CM2.0), through to the less altered Murray (CM2.4/2.5) and Murchison (CM2.5). The chips were crushed and analysed using the crush fast scan method [5]. Polished sections of the samples were studied using BSE imaging, ED X-ray mapping and point analyses in a Zeiss Sigma field-emission SEM operated at 20 kV.

Results and discussion: Methane was detected in all the samples. Concentrations are expressed as moles of methane per gram sample and range from 5.64×10^{-11} to 9.73×10^{-11} (**Table 1**). The 3-sigma detection limit for methane is 5×10^{-14} moles/gram and error bars range from 5 to 14% depending on the individual crush. Our data show that the unaltered CV3 Allende contained the lowest amount of methane, while the most aqueously altered CM sample SCO 06043 (serpentine content of ~88 vol. % [14]) yielded the highest concentration. Murray (serpentine content of 74 vol. % [11]) gave the lowest methane concentration out of the three studied CMs. Murchison, which was the least altered CM in this study (serpentine content of 72 vol. % [11]), only showed slightly lower methane levels compared to the most heavily serpentinised SCO 06043. However, SCO 06043 is also the most shocked sample with a strong petrofabric of flattened chondrule pseudomorphs and oriented fractures (**Fig. 1**) [9], and any methane produced by serpentinisation may be expected to escape through fractures produced by later stage shock and deformation. The loss of methane from CMs has been identified in a previous study by [15] who found evidence from the isotopic composition of CM carbonates and their formation waters that methane was indeed generated during aqueous alteration, but that it had escaped. Nonetheless, our findings of methane in the CMs, including in the highly shocked SCO 06043, shows that at least some gas has been retained. Although the CM parent bodies have a moderate porosity, they have very low permeability [16], and therefore methane and other gases could have been trapped despite later shock fracturing.

Table 1. Alteration, shock stage and moles of methane per gram sample of analysed carbonaceous chondrites.

Sample	Group/ alteration	Shock stage	Moles methane / gram sample
Allende	CV3 [17]	S1 [18]	5.64×10^{-11}
Murchison	CM2.5 [12]	S1/S2 [18]	9.57×10^{-11}
Murray	CM2.4/2.5 [12]	S1 [18]	6.92×10^{-11}
SCO 06043	CM2.0 [12]	>30 GPa [9]	9.73×10^{-11}

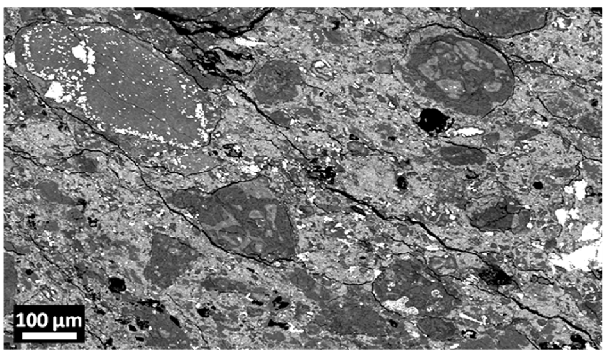

Fig. 1. SEM-BSE micrograph showing petrofabric and oriented fractures in the heavily shocked SCO 06043.

The early CM parent bodies contained all the ingredients for methane production via serpentinisation, i.e. olivine, water and CO_2. Modeling of fluid-rock interactions in carbonaceous chondrites indicates that significant amounts of gas were released during the aqueous alteration, e.g. H_2 from the alteration of silicates, CO_2, and possibly also methane [19]. Our results indicate that the generation of methane could have been a widespread consequence of early planetesimal aqueous alteration, and its preservation in primitive carbonaceous chondrites shows that under appropriate conditions it can be preserved for very long timescales. For example, it has previously been shown that methane is retained also in ancient terrestrial Palaeoproterozoic serpentinites [3]. However, methane can also form by other abiotic processes than serpentinisation, which is highlighted here by the presence of methane also in the CV3 Allende meteorite, perhaps produced via ablation and/or UV radiation [6,7,8].

Conclusions: Our study shows that CM carbonaceous chondrites contain detectable amounts of methane that possibly was generated via aqueous alteration and serpentinisation on the CM parent bodies. SCO 06043 has preserved methane despite being highly shocked, perhaps as a result of the low permeability in CM carbonaceous chondrites.

Furthermore, this study validates the potential that carbonaceous chondrites could bring methane to the surfaces of planets, reiterating that caution needs to be taken when interpreting the remote detection of methane as a signature of life.

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