



# Thermal history of type 3 chondrites from the Antarctic meteorite collection determined by Raman spectroscopy of their polyaromatic carbonaceous matter

Lydie Bonal<sup>a,\*</sup>, Eric Quirico<sup>a</sup>, Laurène Flandinet<sup>a</sup>, Gilles Montagnac<sup>b</sup>

<sup>a</sup> Univ. Grenoble Alpes, Institut de Planétologie et d'Astrophysique de Grenoble, F-38000 Grenoble, France CNRS, IPAG, F-38000 Grenoble, France

<sup>b</sup> Laboratoire de géologie de Lyon, CNRS/INSU UMR5276 - Ens de Lyon - UCB Lyon1, Université de Lyon, 46 allée d'Italie, 69364 Lyon cedex 07, France

Received 15 July 2015; accepted in revised form 11 June 2016; available online 18 June 2016

## Abstract

This paper is focused on the characterization of the thermal history of 151 CV, CO and unequilibrated ordinary chondrites (UOCs) from the NASA Antarctic meteorite collection, using an approach based on the structure of the included polyaromatic carbonaceous matter determined by Raman spectroscopy. 114 out of these 151 chondrites provided Raman spectra of carbonaceous matter and allowing to assign a petrologic type, which mostly reflects the peak temperature experienced by the rock on the parent body. A thorough review of literature shows however that it is not possible to deduce a peak temperature because accurate calibration is not available. Twenty-three new weakly metamorphosed chondrites have been identified: MIL 07671 (CV3.1); DOM 08006 (CO3.0); DOM 03238, MIL 05024, MIL 05104, MIL 07193 (CO3.1); TIL 82408, LAR 06279 (LL3.05-3.1); EET 90628 (L3.0); GRO 06054, QUE 97008 (L3.05), ALHA 77176, EET 90066, LAR 04380, MET 96515, MIL 05050 (L3.1); ALHA 78133, EET 87735, EET 90909, LEW 87208, PRE 95401 (L3.05-3.1); MCY 05218 (H3.05-3.1) and MET 00506 (H3.1). This study confirms that the width of the D band ( $FWHM_D$ ) and the ratio of the peak intensity of the D and G bands ( $I_D/I_G$ ) are the most adapted tracers of the extent of thermal metamorphism in type 3 chondrites. It also unambiguously shows, thanks to the large number of samples, that the width of the G band ( $FWHM_G$ ) does not correlate with the maturity of polyaromatic carbonaceous matter. This parameter is nevertheless very valuable because it shows that Raman spectra of CV chondrites preserve memory of either the metamorphic conditions (possibly oxidation controlled by aqueous alteration) or the nature of the organic precursor. Oxidation memory is our preferred interpretation, however an extensive petrologic characterization of this CV series is required to get firm conclusions. Pre-graphitic carbonaceous matter is reported in seven chondrites and is even the only carbonaceous material detected in the chondrites ALHA 78119 and DAV 92302. This pre-graphitic carbonaceous matter cannot be formed through radiogenic thermal metamorphism without metal catalysis. Shock metamorphism is another possible process for accounting its formation, but it appears less plausible. © 2016 Elsevier Ltd. All rights reserved.

**Keywords:** Thermal metamorphism; CV chondrites; CO chondrites; Ordinary chondrites; Organic matter; Raman spectroscopy

## 1. INTRODUCTION

Chondrites are the most primitive meteorites of our collections and among the most primitive cosmomaterials available in laboratory. Because chondrites did not

\* Corresponding author.

E-mail address: [lydie.bonal@obs.ujf-grenoble.fr](mailto:lydie.bonal@obs.ujf-grenoble.fr) (L. Bonal).

experience melting and igneous differentiation on their asteroidal parent bodies, they largely preserve records of physical and chemical processes in the solar nebula. However, most chondrites experienced secondary processes, such as aqueous alteration, thermal and shock metamorphism, on their parent asteroids (e.g., Krot et al., 2003). Different intensities of these secondary processes have more or less modified the primary properties of the chondritic components (e.g., Brearley and Jones, 1998). A correct interpretation of the modifications induced by these geological processes is indispensable if one wants to understand how the components in chondrites were formed and to identify chondrites as the most suitable for studying nebular processes.

Chondrites experienced a wide range of secondary processing, which are rated by the associated petrologic types ranging from 1 to 6 (Van Schmus and Wood, 1967; McSween, 1979). Type 1 represents a higher degree of aqueous alteration compared with type 2, the distinction being largely based on the abundance of hydrous silicates and oxyhydroxides. Type 1 and 2 chondrites mostly escaped thermal metamorphism (temperature of alteration lower than 150 °C, e.g., Brearley, 2006), although short duration thermal metamorphism, presumably controlled by shocks or solar heating, has been reported (Nakato et al., 2008; Tonui et al., 2014). The sequence from type 3 (commonly called unequilibrated, UOC) to type 6 (commonly called equilibrated) represents an increasing degree of chemical equilibrium, recrystallization and textural evolution, mainly due to thermal metamorphism. Types 4, 5, and 6 chondrites are characterized by the presence of diverse mineralogical assemblages at chemical equilibrium. Mineral thermometers can thus be applied to determine equilibration temperature (e.g., McSween and Patchen, 1989; Johnson and Prinz, 1991; Kessel et al., 2007). Although type 3 chondrites are objects the least modified by secondary processes, they experienced a wide range of thermal metamorphism. Sears et al. (1980) defined a subdivision of the petrologic type 3 in order to mirror this large variation among unequilibrated ordinary chondrites (UOC). The scale was later extended to several groups, including the CV (e.g., Guimon et al., 1995; Bonal et al., 2006), CO carbonaceous chondrites (Scott and Jones, 1990; Sears et al., 1991a; Chizmadia et al., 2002; Bonal et al., 2007) and enstatite chondrites (Zhang et al., 1995; Quirico et al., 2011). A 3.0 petrologic type typically designates meteorites that have experienced very little metamorphism and 3.9 those that have nearly reached the chemical equilibrium in some minerals, characteristic to type 4 (Van Schmus and Wood, 1967; Dodd et al., 1967). Due to the presence of a mixture of unequilibrated minerals, the use of mineral-equilibration thermometers is obviously not straightforward in type 3 chondrites. Moreover, in most cases thermal metamorphism was associated with the circulation of fluids on the asteroidal parent body. Aqueous alteration can result in the perturbation of some metamorphic tracers, leading to an erroneous evaluation of the metamorphic degree of an object. Bonal et al. (2006) have indeed shown that the petrologic types of oxidized CVs based on induced thermoluminescence (ITL) are systematically underestimated,

demonstrating that aqueous alteration strongly disturbs the thermoluminescence sensitivity as feldspars are dissolved by water during the aqueous alteration process. Based on the same metamorphic tracers, a direct comparison of the metamorphic grade of chondrites obtained through thermoluminescence sensitivity from different chemical groups might thus not be straightforward. Terrestrial weathering is another process that could complicate the interpretation of various tracers. Lastly, brecciation was probably experienced by a large number of chondrites (e.g., by >40% of all unequilibrated ordinary chondrites; Sears et al., 1991b). Subregions having experienced distinct metamorphic histories might be adjacent in the same meteorite.

The degree of structural order of the polyaromatic carbonaceous matter present in the matrix of chondrites reflects the thermal history of type 3 chondrites. Indeed, this metamorphic tracer has been successfully applied on series of UOC (Quirico et al., 2003), CV (Bonal et al., 2006) and CO (Bonal et al., 2007) and enstatite (Quirico et al., 2011) chondrites. These studies were all based on Raman spectroscopy on raw matrix grains or polished and thin sections. Busemann et al. (2007) applied Raman spectroscopy on chemically extracted carbonaceous material from a large series of types 1–3 chondrites, and reports implications on thermal metamorphism and terrestrial weathering. A similar approach was also followed for Stardust grains (Sandford et al., 2006), Interplanetary Dust Particles (e.g., Davidson et al., 2012; Starkey et al., 2013) and Antarctic micrometeorites (e.g., Dobrica et al., 2011).

Since 1977, meteorites have been collected every year by the National Science Foundation and NASA funded science teams operating out of the McMurdo or South Pole Stations. The ANtarctic Search for METeorites (ANSMET) teams collection efforts in the last 30 years have recovered over 16,000 meteorite samples. They are returned frozen to NASA Johnson Space Center (JSC) for initial processing and characterization (NASA Antarctic Meteorites website). The Antarctic meteorites collection is invaluable to any cosmochemist. A detailed evaluation of their post-accretion history is required to provide a good context in the interpretation of any mineralogical, chemical, and petrological characteristics. The Antarctic meteorites represent a very large collection of precious samples, some of them being present in only small amount. It is thus necessary to use techniques that are easy to apply and adapted to small quantities to characterize the secondary history of all of these samples.

In the present paper we consider the structural order of polyaromatic carbonaceous material, as evaluated by Raman spectroscopy, as a tracer of the thermal history of type 3 chondrites (UOC, CO, and CV) of 151 chondrites from the Antarctic meteorites collection. Our objectives are to: (i) provide a reliable evaluation and interclassification of the thermal history by attributing petrologic types to these type 3 Antarctic chondrites, and (ii) give all the necessary details on the context and the method to be applied to evaluate the petrologic types of any new type 3 chondrites by Raman spectroscopy. To ease the reading of the present paper, most of the technical discussions on the

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