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# Light element geochemistry of the Tagish Lake CI2 chondrite: Comparison with CI1 and CM2 meteorites

M. M. GRADY[1]*, A. B. VERCHOVSKY[2], I. A. FRANCHI[2], I. P. WRIGHT[2] AND C. T. PILLINGER[2]

[1]Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K.
[2]PSSRI, The Open University, Walton Hall, Milton Keynes MK7 6AA, U.K.
*Correspondence author's e-mail address: M.Grady@nhm.ac.uk

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**Abstract**–We have studied the carbon and nitrogen stable isotope geochemistry of a small pristine sample of the Tagish Lake carbonaceous chondrite by high-resolution stepped-combustion mass spectrometry, and compared the results with data from the Orgueil (CI1), Elephant Moraine (EET) 83334 (CM1) and Murchison (CM2) chondrites. The small chip of Tagish Lake analysed herein had a higher carbon abundance (5.81 wt%) than any other chondrite, and a nitrogen content (~1220 ppm) between that of CI1 and CM2 chondrites. Owing to the heterogeneous nature of the meteorite, the measured carbon abundance might be artificially high: the carbon inventory and whole-rock carbon isotopic composition ($\delta^{13}C \approx +24.4$‰) of the chip was dominated by $^{13}C$-enriched carbon from the decomposition of carbonates (between 1.29 and 2.69 wt%; $\delta^{13}C \approx +67$‰ and $\delta^{18}O \approx +35$‰, in the proportions ~4:1 dolomite to calcite). In addition to carbonates, Tagish Lake contains organic carbon (~2.6 wt%, $\delta^{13}C \approx -9$‰; 1033 ppm N, $\delta^{15}N \approx +77$‰), a level intermediate between CI and CM chondrites. Around 2% of the organic material is thermally labile and solvent soluble. A further ~18% of the organic species are liberated by acid hydrolysis. Tagish Lake also contains a complement of presolar grains. It has a higher nanodiamond abundance (approximately 3650–4330 ppm) than other carbonaceous chondrites, along with ~8 ppm silicon carbide. Whilst carbon and nitrogen isotope geochemistry is not diagnostic, the data are consistent with classification of Tagish Lake as a CI2 chondrite.

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## INTRODUCTION

The Tagish Lake meteorite fell in Canada, close to the British Columbia/Yukon border on the morning of 2000 January 18; a bright fireball and a prominent dust tail accompanied its atmospheric entry. The following week, several pieces of meteorite, weighing ~1 kg in total were recovered from the frozen surface of the Taku Arm branch of Tagish Lake. The material remained frozen during subsequent transport and storage at the NASA Johnson Space Center curatorial facility. These specimens have been described as "pristine" material, to distinguish them from specimens collected during April and May, following intense snowfall in the Yukon/British Columbia area. Material from this second collection sequence is described as "degraded", mainly because of its exposure to meltwater. Initial petrographic examination of the "pristine" meteorite indicated that it was a matrix- and carbonate-rich carbonaceous chondrite (Zolensky *et al.*, 2000). Compared with CI1 chondrites, Tagish Lake also had elevated carbon abundances (Grady *et al.*, 2000). Tagish Lake was subsequently provisionally classified as a CI2 chondrite (Brown *et al.*, 2000).

CI and CM chondrites are the two meteorite classes that contain the highest abundances of indigenous organic material. The organic matter is a mixture of soluble and insoluble species, simple and complex, aliphatic, heterocyclic and aromatic (*e.g.*, Cronin and Chang, 1993). A major component of the organics is thought to be derived directly from interstellar organic molecules (*e.g.*, Alexander *et al.*, 1993); parent-body processes (mainly aqueous) have altered the remainder. Up until the fall of Tagish Lake, CI chondrites (named for the type specimen Ivuna) numbered only five in total and were all assigned to petrologic type 1. The implication of classification "CI1" derives from the scheme first outlined by McSween (1979), in which the extent of hydrous alteration experienced by carbonaceous chondrites increased from type 3 to type 1. On the basis of studies of oxygen isotopes in components of carbonaceous chondrites, it has been inferred that CI1 chondrites were altered in a warmer and wetter environment than CM2 (Clayton and Mayeda, 1999).

There are very few CM1 chondrites: one subgroup with this classification has four members that are believed to be slightly metamorphosed, and thus dehydrated, CI1 chondrites (*e.g.*, Akai, 1990; Paul and Lipschutz, 1990; Clayton and Mayeda, 1999). In contrast, Elephant Moraine (EET) 83334 is a CM chondrite that has been more heavily altered by fluids than most CM2 chondrites and has no anhydrous silicates, exhibiting only relic calcium-aluminum-rich inclusions (CAIs) (Zolensky *et al.*, 1997). Tagish Lake is, thus far, the only CI2 chondrite. It contains chondrules and at least one, very large, altered CAI (Brown *et al.*, 2000; Zolensky *et al.*, 2000). The implication of classification as CI2 is that Tagish Lake is from the same parent body as CI chondrites, but less aqueously processed than CI1 chondrites. The variations in texture, modal mineralogy, hydration state and light element stable isotope composition exhibited by CI and CM chondrites are an indication that the CI and CM asteroidal parents have been subject to a wider range of hydrous processing than perhaps had been envisioned previously.

Analysis of Tagish Lake, and comparison of its carbon and nitrogen light element geochemistry with that of the Orgueil (CI1), EET 83334 (CM1) and Murchison (CM2) chondrites, is a step towards unravelling the extent, sequence and duration of fluid activity on asteroids. This paper is the first stage in a complete and thorough analysis of organics in Tagish Lake (*e.g.*, Gilmour *et al.*, 2001; Pizzarello, 2001). A small chip (<10 mg) whole-rock meteorite was made available for this analysis, intending that it would act as a pathfinder study for subsequent, more specialised studies. Results are compared with new analyses of similar amounts of the Orgueil (CI1) and Murchison (CM2) chondrites, analyses undertaken employing identical protocols and instrumentation to those used for Tagish Lake.

## EXPERIMENTAL

The chip of pristine Tagish Lake was carefully broken into two pieces; one of which was preserved for replicate analyses, if required. The remaining material was broken into two chips, one for measurement of carbon abundance and isotopic composition, the second for determination of nitrogen and noble gas systematics. The analytical technique employed was that of high-resolution stepped-combustion mass spectrometry (HR-SC-MS), undertaken using the Open University's MS86 static vacuum system for carbon (Yates *et al.*, 1992) and Finesse for nitrogen (Verchovsky *et al.*, 1997).

Small chips of material (~1 mg for carbon, 4.4 mg for nitrogen) were wrapped in degassed high-purity platinum foil. They were heated in incremental steps from room temperature to 1400 °C. Each heating step lasted for the same fixed time, and took place in the presence of excess oxygen gas derived from the equilibrium decomposition of copper (II) oxide. A hot platinum catalyst within the combustion vessel ensured that volatile species were combusted to $CO_2$, even at the lowest temperature steps of the experiment. Byproducts of combustion ($SO_2$, $H_2O$, *etc.*) were separated from the gases of interest ($CO_2$, $N_2$) by a series of cold traps and fingers, following which the gases were quantified and their isotopic compositions determined. Carbon abundance was measured by two methods: using a capacitance manometer within a known volume, and also from calibration of the MS86 ion beam current. The performance of the system for measurement of sample yields greater than ~10 ng is better than ±0.5‰ in $\delta^{13}C$ and ±1% in the yield (Yates *et al.*, 1992). Carbon isotopic compositions were determined relative to a laboratory $CO_2$ standard gas calibrated against NBS standard materials; results are quoted relative to the international PDB standard. Nitrogen abundances were determined from the ion beam current in the Finesse mass spectrometer. For sample sizes greater than ~2 ng, errors on abundance measurements were less than ±5% of the yield, and nitrogen isotopic compositions (measured against air) were accurate to ±2‰.

A second, larger, sample of pristine Tagish Lake was made available for high-precision organic carbon analysis by chromatographic methods (Gilmour *et al.*, 2001); ~150 mg from this sample was powdered, to provide material for carbonate analysis. Two 30 mg aliquots were taken from the reservoir, then progressively dissolved in 100% orthophosphoric acid ($H_3PO_4$), following the protocol outlined in Grady *et al.* (1988). Separate dissolution temperatures of 25 and 75 °C allowed sequential dissolution of calcite, then dolomite and breunnerite in the meteorite. The carbon and oxygen isotopic compositions of the carbonates were determined using a GEO-2020 mass spectrometer (PDZ Europa), to a precision of ±0.5‰; carbonate abundance was quantified by measurement in a capacitance manometer of the $CO_2$ released by the acid.

The residue remaining following dissolution was recovered after several cycles of washing with distilled and de-ionised water, interspersed with agitation and centrifuging. Weight-loss on dissolution was ~87%, implying that the acid treatment had dissolved most of the silicate minerals in addition to the carbonates. The $H_3PO_4$-resistant residue was also analysed for carbon and nitrogen by HR-SC-MS.

## TOTAL CARBON AND NITROGEN

Carbon results from stepped combustion of the 1.017 mg chip of pristine Tagish Lake are shown in Fig. 1 and given in Table 1; results from nitrogen analysis of the 4.400 mg chip are given in Fig. 2 and Table 2. The total carbon yield was 5.81 wt%, with $\delta^{13}C \approx +24.4‰$. Comparison with whole-rock data from CI and CM chondrites (Kerridge, 1985) shows that the carbon yield is higher than from CI1 and CM2 chondrites (Fig. 3a,c). The total $\delta^{13}C$ is also elevated compared with typical values for both CI and CM groups (Fig. 3b,c and Table 1), a reflection of the abundant $^{13}C$-rich carbonates that characterise Tagish Lake (see later section). Tagish Lake has

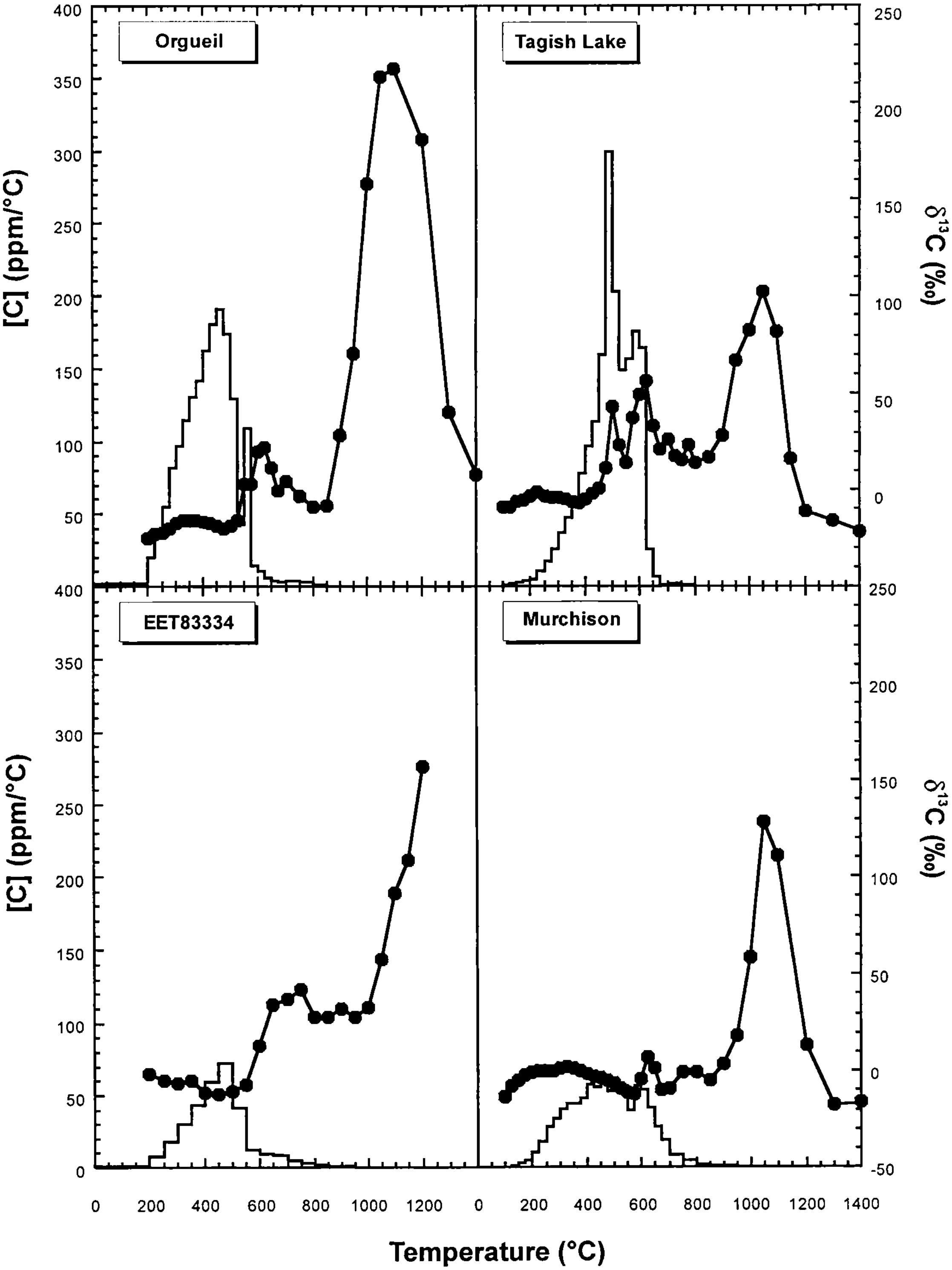

FIG. 1. Stepped combustion of (a) Orgueil, (b) Tagish Lake, (c) EET 83334 and (d) Murchison. The yield of carbon released at each step of the experiment (in ppm/°C) is given as a histogram; the corresponding isotopic composition is plotted as dots joined by a line. Errors in $\delta^{13}C$ are less than the size of the symbol.

TABLE 1. Carbon data from stepped combustion.

| | Tagish Lake 1.017 mg | | TL residue* 0.042 mg | | Orgueil 0.774 mg | | Murchison 1.0332 mg | | EET 83334 2.261 mg | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp. (°C) | [C] (ppm) | $\delta^{13}C$ (‰) | [C] (ppm) | $\delta^{13}C$ (‰) | [C] (ppm) | $\delta^{13}C$ (‰) | [C] (ppm) | $\delta^{13}C$ (‰) | [C] (ppm) | $\delta^{13}C$ (‰) |
| 100 | 57.8 | –9.2 | – | – | – | – | 4.5 | –13.4 | – | – |
| 125 | 36.4 | –9.4 | – | – | – | – | 11.7 | –7.9 | – | – |
| 150 | 62.6 | –6.4 | – | – | – | – | 37.7 | –4.9 | – | – |
| 175 | 79.2 | –5.5 | – | – | – | – | 75.2 | –2.3 | – | – |
| 200 | 106.8 | –3.1 | 330.0 | –21.3 | 485.1 | –25.4 | 129.5 | –1.0 | 221.3 | –1.5 |
| 225 | 160.7 | –1.4 | – | – | 505.9 | –23.5 | 250.8 | –0.2 | – | – |
| 250 | 316.3 | –3.5 | 639.8 | –17.3 | 874.2 | –22.1 | 454.7 | –0.2 | 361.5 | –4.5 |
| 275 | 535.0 | –4.4 | – | – | 1374.2 | –20.1 | 718.5 | 0.4 | – | – |
| 300 | 798.3 | –3.9 | 1746.9 | –11.8 | 2041.1 | –17.5 | 858.3 | 1.7 | 896.9 | –6.0 |
| 325 | 1151.5 | –4.8 | – | – | 2428.8 | –16.2 | 1008.6 | 2.5 | – | – |
| 350 | 1476.6 | –6.1 | 4426.2 | –10.6 | 2862.8 | –16.0 | 1098.5 | 1.7 | 1510.1 | –4.6 |
| 375 | 1924.9 | –6.7 | – | – | 3261.1 | –16.2 | 1108.2 | 0.2 | – | – |
| 400 | 2443.9 | –5.0 | 7896.8 | –13.7 | 3542.8 | –17.0 | 1190.0 | –1.4 | 2153.7 | –11.0 |
| 425 | 3021.7 | –1.8 | 4534.1 | –20.3 | 4054.1 | –17.8 | 1435.4 | –2.7 | – | – |
| 450 | 3566.3 | +0.7 | 2186.7 | –21.8 | 4500.1 | –19.2 | 1390.2 | –3.7 | 2956.0 | –11.8 |
| 475 | 4980.7 | +11.5 | 1100.9 | –21.6 | 4769.1 | –20.2 | 1455.6 | –5.0 | – | – |
| 500 | 9368.7 | +43.1 | 661.7 | –23.6 | 4355.3 | –19.1 | 1309.1 | –6.5 | 3631.7 | –10.4 |
| 525 | 6355.9 | +23.4 | 288.6 | –17.8 | 3236.0 | –15.8 | 1371.5 | –8.9 | – | – |
| 550 | 4678.5 | +14.5 | 148.3 | –15.4 | 1069.9 | +2.8 | 1401.4 | –11.1 | 2094.6 | –7.0 |
| 575 | 4897.8 | +37.7 | 75.6 | –20.5 | 2726.7 | +2.9 | 986.3 | –12.2 | – | – |
| 600 | 5501.1 | +49.7 | 75.9 | –23.2 | 344.2 | +19.8 | 1403.3 | –4.5 | 619.9 | +13.7 |
| 625 | 5124.3 | +56.2 | – | – | 270.3 | +22.2 | 1344.4 | +7.3 | – | – |
| 650 | 783.8 | +33.0 | 73.1 | –24.8 | 141.0 | +11.7 | 1043.3 | +1.4 | 489.9 | +34.3 |
| 675 | 221.3 | +21.2 | – | – | 92.5 | –0.7 | 710.5 | –9.5 | – | – |
| 700 | 40.8 | +26.4 | 66.8 | –26.4 | 77.0 | +4.1 | 463.9 | –9.3 | 408.8 | +37.4 |
| 725 | 58.3 | +18.0 | – | – | – | – | – | – | – | – |
| 750 | 52.7 | +15.4 | 78.0 | –25.6 | 181.8 | –3.4 | 442.2 | –0.9 | 221.1 | +42.4 |
| 775 | 32.3 | +23.1 | – | – | – | – | – | – | – | – |
| 800 | 36.5 | +14.2 | 17.7 | –26.3 | 158.3 | –8.8 | 220.0 | –0.6 | 135.1 | +28.6 |
| 850 | 32.1 | +16.9 | – | – | 29.7 | –8.5 | 106.3 | –4.9 | 81.1 | +28.0 |
| 900 | 31.0 | +28.3 | 75.1 | –23.3 | 24.7 | +28.2 | 66.9 | +3.4 | 60.8 | +32.6 |
| 950 | 12.0 | +67.2 | – | – | 13.4 | +70.8 | 40.4 | +18.5 | 49.8 | +28.5 |
| 1000 | 30.2 | +82.5 | 52.7 | –16.5 | 13.2 | +157.8 | 27.0 | +58.5 | 27.4 | +33.4 |
| 1050 | 27.3 | +102.1 | – | – | 15.0 | +213.2 | 21.4 | +128.6 | 11.8 | +57.9 |
| 1100 | 23.3 | +81.5 | 44.4 | +18.8 | 9.2 | +217.5 | 13.6 | +110.5 | 12.7 | +91.5 |
| 1150 | 11.0 | +16.1 | – | – | – | – | – | – | 14.4 | +108.2 |
| 1200 | 20.7 | –10.9 | 119.3 | +19.9 | 5.0 | +180.9 | 8.7 | +13.5 | 5.9 | +157.0 |
| 1300 | 22.5 | –15.8 | 231.9 | –27.2 | 0.9 | +40.0 | 11.3 | –17.2 | – | – |
| 1400 | 37.0 | –21.7 | 61.8 | –31.5 | 0.2 | +7.7 | 21.2 | –16.4 | – | – |
| Total | 5.81% | +24.4 | 2.49% | –16.0 | 4.35% | –15.2 | 2.22% | –2.8 | 1.60% | –3.8 |

*Residue from orthophosphoric acid dissolution; figures corrected for 87% weight loss on dissolution, and quoted relative to whole-rock values.

a nitrogen abundance between CI and CM, with an isotopic composition more $^{15}N$-enriched than CI or CM chondrites: [N] = 1218.3 ppm; $\delta^{15}N \approx +67‰$ (Fig. 3a,b,d and Table 2). A word of caution is expressed: although an attempt was made to select a "typical" portion of Tagish Lake, avoiding any obvious clasts or inclusions, it is almost certain that sample heterogeneity at the milligram level may be reflected in lower carbon or nitrogen abundances in other splits of the meteorite.

Examination of the carbon release profile (Fig. 1) shows that there are several carbon-bearing components present, distinguished either by peaks in the yield histogram, or by maxima and minima in isotopic composition. The nitrogen yield histogram (Fig. 2) shows one broad release between 200 and 800 °C, centred at ~500 °C. Across this temperature range, there are several nitrogen components present, as indicated by variations in $\delta^{15}N$ between +40 and +90‰.

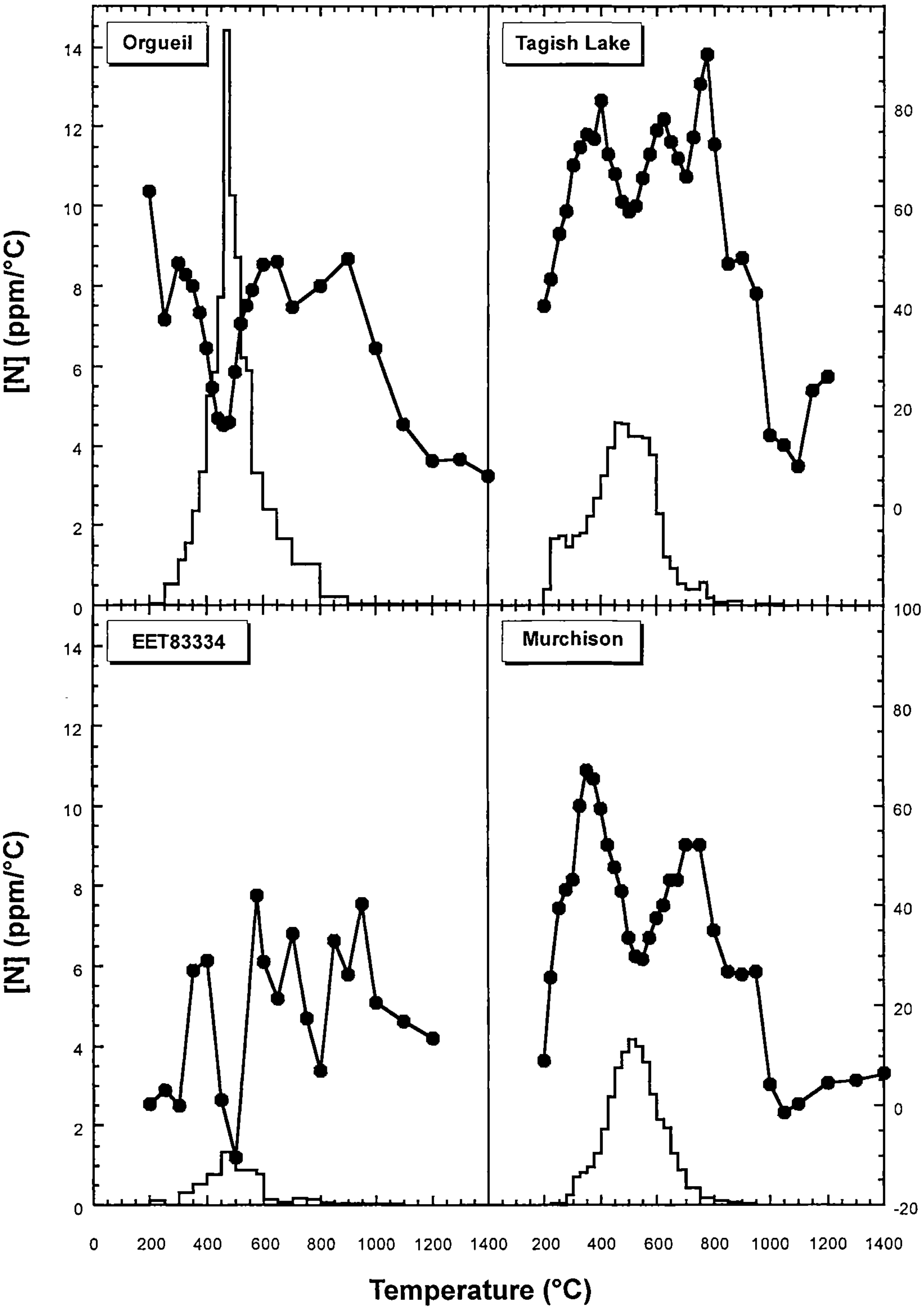

FIG. 2. Stepped combustion of (a) Orgueil, (b) Tagish Lake, (c) EET 83334 and (d) Murchison. The yield of nitrogen released at each step of the experiment (in ppm/°C) is given as a histogram; the corresponding isotopic composition is plotted as dots joined by a line. Errors in $\delta^{15}N$ are less than the size of the symbol.

TABLE 2. Nitrogen data from stepped combustion.

| Temp. (°C) | Tagish Lake 4.400 mg | | Tagish Lake residue* 0.275 mg | | Orgueil 2.938 mg | | Murchison 4.867 mg | | EET 83334 1.305 mg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | [N] (ppm) | $\delta^{15}N$ (‰) | [N] (ppm) | $\delta^{15}N$ (‰) | [N] (ppm) | $\delta^{15}N$ (‰) | [N] (ppm) | $\delta^{15}N$ (‰) | [N] (ppm) | $\delta^{15}N$ (‰) |
| 200 | 3.3 | +40 | 2.3 | +48 | 0.8 | +63 | 1.2 | +9 | 1.9 | 0 |
| 225 | 8.7 | +45 | – | – | – | – | 0.5 | +26 | – | – |
| 250 | 37.8 | +54 | 8.8 | +69 | 2.8 | +37 | 0.6 | +39 | 5.1 | +3 |
| 275 | 39.2 | +59 | – | – | – | – | 1.1 | +43 | – | – |
| 300 | 32.8 | +68 | 116.5 | +82 | 26.7 | +48 | 5.9 | +45 | 0.0 | – |
| 325 | 39.7 | +72 | – | – | 28.2 | +46 | 17.5 | +60 | – | – |
| 350 | 41.1 | +74 | 529.6 | +55 | 38.9 | +44 | 20.3 | +67 | 15.6 | +27 |
| 375 | 50.2 | +74 | – | – | 59.5 | +39 | 24.1 | +66 | – | – |
| 400 | 61.0 | +81 | 164.3 | –2 | 83.7 | +32 | 32.6 | +60 | 27.4 | +29 |
| 425 | 74.1 | +70 | – | – | 105.2 | +24 | 47.5 | +52 | – | – |
| 450 | 89.7 | +67 | 28.9 | –10 | 193.9 | +17 | 67.8 | +48 | 38.6 | +1 |
| 475 | 103.9 | +61 | – | – | 365.1 | +17 | 86.8 | +43 | – | – |
| 500 | 103.4 | +59 | 9.6 | –33 | 204.9 | +27 | 96.2 | +34 | 67.3 | –11 |
| 525 | 95.8 | +60 | – | – | 174.2 | +36 | 103.7 | +30 | – | – |
| 550 | 96.1 | +66 | 3.7 | –162 | 241.6 | +42 | 99.3 | +29 | – | – |
| 575 | 95.4 | +71 | – | – | – | – | 90.0 | +34 | 67.1 | +42 |
| 600 | 85.7 | +75 | 1.9 | –105 | 132.1 | +48 | 70.0 | +37 | 19.7 | +29 |
| 625 | 52.4 | +77 | – | – | – | – | 53.4 | +40 | – | – |
| 650 | 27.4 | +73 | – | – | 119.4 | +49 | 48.8 | +45 | 6.9 | +22 |
| 675 | 20.6 | +70 | – | – | – | – | 32.5 | +45 | – | – |
| 700 | 12.4 | +66 | 2.8 | –81 | 82.5 | +40 | 22.4 | +52 | 4.5 | +34 |
| 725 | 9.0 | +74 | – | – | – | – | – | – | – | – |
| 750 | 9.1 | +84 | – | – | – | – | 21.2 | +52 | 8.5 | +18 |
| 775 | 12.6 | +91 | – | – | – | – | – | – | – | – |
| 800 | 4.0 | +72 | 1.8 | –47 | 101.8 | +44 | 9.6 | +35 | 7.0 | +7 |
| 850 | 3.8 | +49 | – | – | – | – | 5.1 | +27 | 4.4 | +33 |
| 900 | 4.3 | +50 | 1.2 | –43 | 21.2 | +49 | 3.0 | +26 | 2.8 | +26 |
| 950 | 0.7 | +43 | – | – | – | – | 1.6 | +27 | 1.3 | +40 |
| 1000 | 1.4 | +14 | 1.1 | –61 | 4.6 | +32 | 1.1 | +4 | 1.7 | +21 |
| 1050 | 1.2 | +12 | – | – | – | – | 0.7 | –1 | – | – |
| 1100 | 0.5 | +8 | 1.2 | –33 | 3.6 | +16 | 0.5 | 0 | 3.4 | +17 |
| 1150 | 0.5 | +23 | – | – | – | – | – | – | – | – |
| 1200 | 0.5 | +26 | 2.6 | +39 | 3.8 | +9 | 0.6 | +5 | 2.1 | +14 |
| 1300 | – | – | 2.1 | +43 | 3.2 | +9 | 0.7 | +5 | – | – |
| 1400 | – | – | 2.6 | +40 | 1.9 | +6 | 0.8 | +7 | – | – |
| Total | 1218.3 | +67 | 880.8 | +43 | 1999.6 | +32 | 966.9 | +41 | 285.4 | +17 |

*Residue from orthophosphoric acid dissolution; figures corrected for 87% weight loss on dissolution, and quoted relative to whole-rock values.

Carbon and nitrogen combusting across different temperature intervals can be ascribed to discrete components, although overlap in combustion temperature requires deconvolution of the components. The major carbon-bearing components in CI and CM chondrites are (1) organic species and (2) carbonates. A volumetrically minor, but isotopically significant additional component is carbon from exotic grains (predominantly diamonds, graphite and silicon carbide). Organic species generally combust below ~600 °C, and to some extent, stepped combustion distinguishes between different parts of the organic complex in meteorites. The free organics and the more thermally labile side-chain components are liberated at lower temperatures ($T <$ ~225 °C) than that at which the core macromolecule combusts ($T \approx$ 400–600 °C). In order to use stepped-combustion data to quantify the amount of organic material present in CI and CM chondrites, corrections have to be applied for the presence of carbon from non-organic sources. This is because at temperatures above ~375 °C, carbon both

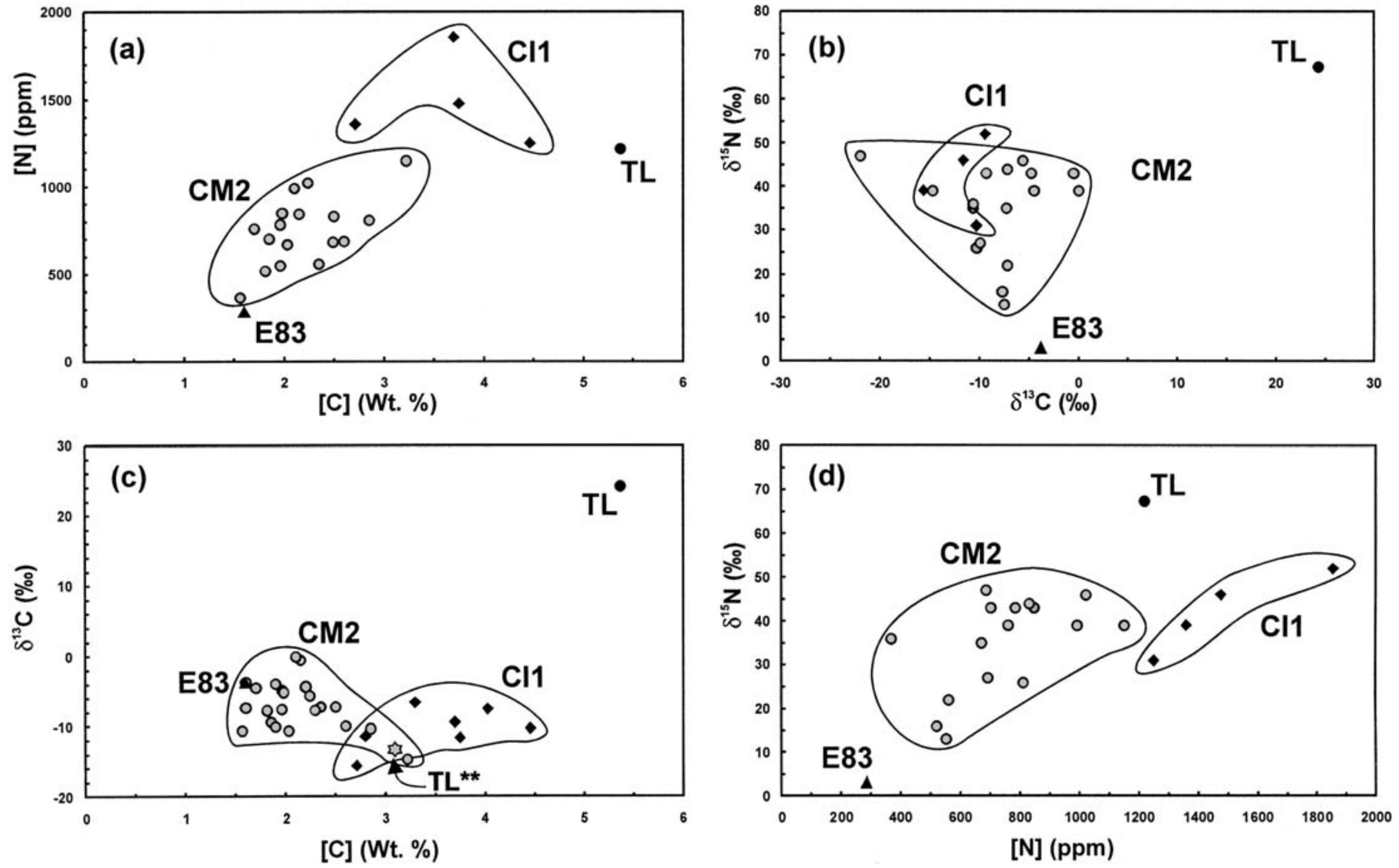

FIG. 3. Comparison of whole-rock carbon and nitrogen abundances and isotopic compositions of Tagish Lake with CI and CM chondrites. Whole-rock data from Kerridge (1985).

from decomposition of carbonates and from combustion of nanodiamonds is mixed in with that from the organic compounds. The problem is particularly acute for Tagish Lake, where carbonates are so abundant. However, knowing the $\delta^{13}C$ of the carbonates (from acid dissolution) and $\delta^{13}C$ of nanodiamonds (from other studies, such as Russell *et al.*, 1996), it is possible to calculate how much carbon combusting above 350 °C is from organic species, and how much is from other sources. Full details of how the carbon data were deconvoluted into different components, and the limits associated with the calculation, are given in the appendix.

## ORGANIC SPECIES (TEMPERATURE LESS THAN 600 °C)

There have been many studies of organic material in CI and CM chondrites; published reviews stand as markers in the evolution of ideas about its origin and history (*e.g.*, Hayes, 1967; Hayatsu and Anders, 1981; Cronin and Chang, 1993). The gross "composition" of the organic material in Murchison has been calculated as $C_{100}H_{70}N_{3.1}O_{16}$ (Hayatsu *et al.*, 1977) and $C_{100}H_{53}N_{2.9}$ (Cody *et al.*, 1999), whilst that of Orgueil is $C_{100}H_{76}N_{1.9}O_{21}$ (quoted in Hayatsu *et al.*, 1977), figures which imply a range of possible atomic C/N ratios from ~53 for CI and ~33 for CM chondrites. The structure of the organic complex can be approximated as a central core of aromatic and heterocyclic molecules bridged together by aliphatic chains. The macromolecular core is acid- and solvent-insoluble; its structure has been investigated using analytical processes such as hydrous pyrolysis, which allows the links between the more condensed molecules to be broken. Associated with the macromolecule are less complex species (alkanes, organic acids, amines, *etc.*) that form side chains off the central core; although these species are solvent-insoluble, they are released by mild thermal and hydrous processing (Sephton *et al.*, 1998, 2000). Free organic compounds also occur in carbonaceous chondrites. This soluble component comprises a variety of species, including amino and carboxylic acids, alkanes, ketones, nitrogen heterocyclics, *etc.* (*e.g.*, summarised by Cronin and Chang, 1993). It is known from previous studies that solvent-extractable material is enriched in $^{13}C$ relative to the non-volatile fraction, with $\delta^{13}C$ as high as approximately +45‰ for some of the amino acids (Pizzarello *et al.*, 1991) and up to +25‰ for carboxylic acids (Yuen *et al.*, 1984). The corresponding nitrogen isotopic compositions are also isotopically heavy, with $\delta^{15}N$ reaching up to +90‰ in amino acids (Epstein *et al.*, 1987).

Following correction for contributions from carbonates and presolar grains (see appendix), approximately half of the total carbon and nitrogen in Tagish Lake occurs as organic species. Figures 4 and 5 are expanded versions of the low-temperature data for Tagish Lake, to enable results for the organic compounds to be seen more clearly. Material combusting below ~350 °C is not affected by interference from other species, and is considered to be organic material alone. There are two trends that can be seen in the carbon isotope data. As temperature increases from room temperature to 225 °C, there is a steady increase in $\delta^{13}$C from –10 to –1‰. $\delta^{13}$C then falls progressively to a minimum of –6‰ at ~350 °C. In contrast, nitrogen exhibits a practically monotonic increase in $\delta^{15}$N with temperature. Nitrogen isotopic composition rises from $\delta^{15}$N ≈ +40 to +45‰ to $\delta^{15}$N ≈ +70‰ between 225 and 350 °C. All $\delta^{13}$C and $\delta^{15}$N values are within the range shown by organic materials in CI and CM chondrites (*e.g.*, Cronin and Chang, 1993).

Above ~375 °C, carbon from organic species is swamped by carbon from decomposition of the abundant carbonates, as indicated by elevated $\delta^{13}$C values (Table 1 and Fig. 4). Modelling release of carbon from species combusting below 600 °C (see appendix) gives a total organic carbon content for Tagish Lake of between 2.49 and 2.57 wt%, with $\delta^{13}$C between –8.8 and –9.1‰ (the ranges come from the method by which organic carbon abundance is deconvoluted from nanodiamond and carbonate abundances, see appendix). The yield of organic nitrogen is 1033 ppm with $\delta^{15}$N ≈ +77‰ (Table 3).

In order to compare organic carbon and nitrogen in Tagish Lake with that in CI and CM chondrites, samples of Orgueil (CI1) and Murchison (CM2) were analysed by HR-SC-MS under identical conditions. Data from a previous study of EET 83334 (CM1; Zolensky *et al.*, 1997) are included to complete a suite of CI and CM chondrites (Figs. 4 and 5; Table 3). Murchison and Tagish Lake both show similar patterns in variation of $\delta^{13}$C with temperature: a gradual increase in $\delta^{13}$C up to 225 °C, followed by a progressive decrease to lower $\delta^{13}$C values (data for Orgueil and EET 83334 were acquired at insufficient temperature resolution, so any equivalent pattern is not detectable). Variations in $\delta^{13}$C indicate that a mixture of species is burning across the temperature range. For Murchison, Tagish Lake and EET 83334, the combined $\delta^{13}$C of these species is higher than that which combusts at $T > 225$ °C (Table 3). A slightly lower percentage of the total organic carbon in Tagish Lake is thermally labile (2.1%), compared with that in Orgueil (2.5%), Murchison (3.0%) and EET 83334 (2.9%). In contrast, the amount of labile nitrogen in Tagish Lake is higher than in Orgueil and Murchison, as indicated both by a higher nitrogen abundance (12 ppm) and lower atomic C/N ratio (~49). The elevated $\delta^{15}$N of the component (approximately +50‰) precludes rationalisation of the excess nitrogen as a terrestrial contaminant. It seems that nitrogen-bearing organic species in Tagish Lake are more prevalent than in the other chondrites. If material has been lost by processing on Tagish Lake's asteroidal parent, then the organic species that have been removed were nitrogen-poor (*e.g.*, such as carboxylic rather than amino acids or aliphatics rather than N-bearing heterocyclics).

It is possible that the inventories of low-temperature organic species in both Orgueil and EET 83334 have been somewhat modified during their terrestrial lifetimes (138 years in

TABLE 3. Organic carbon in carbonaceous chondrites.

| | | [C] (%) | $\delta^{13}$C (‰) | %$C_{vol}$* | [N] (ppm) | $\delta^{15}$N (‰) | %$N_{vol}$* | C/N† (at) |
|---|---|---|---|---|---|---|---|---|
| **Total organic carbon‡ (temperature less than 600 °C)** | | | | | | | | |
| Orgueil | CI1 | 3.96 | –17.3 | – | 1645 | +48 | – | 28 |
| Tagish Lake§ | CI2 | 2.49 to 2.57 | –8.8 to –9.1 | – | 1033 | +77 | – | 28–29 |
| TL residue§,# | CI2 | 1.98 to 2.05 | –11.1 to –12.0 | – | 844 | +58 | – | 27–28 |
| EET 83334 | CM1 | 1.35 | –9.0 | – | 250 | +44 | – | 63 |
| Murchison | CM2 | 1.71 | –3.2 | – | 762 | +51 | – | 26 |
| **Low-temperature component (temperature less than 225 °C)** | | | | | | | | |
| Orgueil | CI1 | 0.10 | –24.4 | 2.50 | 2.3 | +47 | 0.14 | 503 |
| Tagish Lake | CI2 | 0.05 | –4.5 | 2.12 | 12.0 | +44 | 1.16 | 49 |
| EET 83334 | CM1 | 0.04 | –2.8 | 2.91 | 4.5 | +2 | 1.91 | 104 |
| Murchison | CM2 | 0.05 | –1.3 | 2.98 | 1.6 | +14 | 0.22 | 372 |

*Percentage of total carbon or nitrogen present as the most thermally labile species.

†Atomic carbon to nitrogen ratio.

‡Corrected for nanodiamonds and carbonates (see appendix for details of the calculation).

§The range of carbon contents and $\delta^{13}$C values for Tagish Lake comes from the method by which the data are corrected for contributions from nanodiamonds and carbonate. See appendix for full details.

#Residue from orthophosphoric acid dissolution; figures corrected for 87% weight loss on dissolution, and quoted relative to whole-rock values.

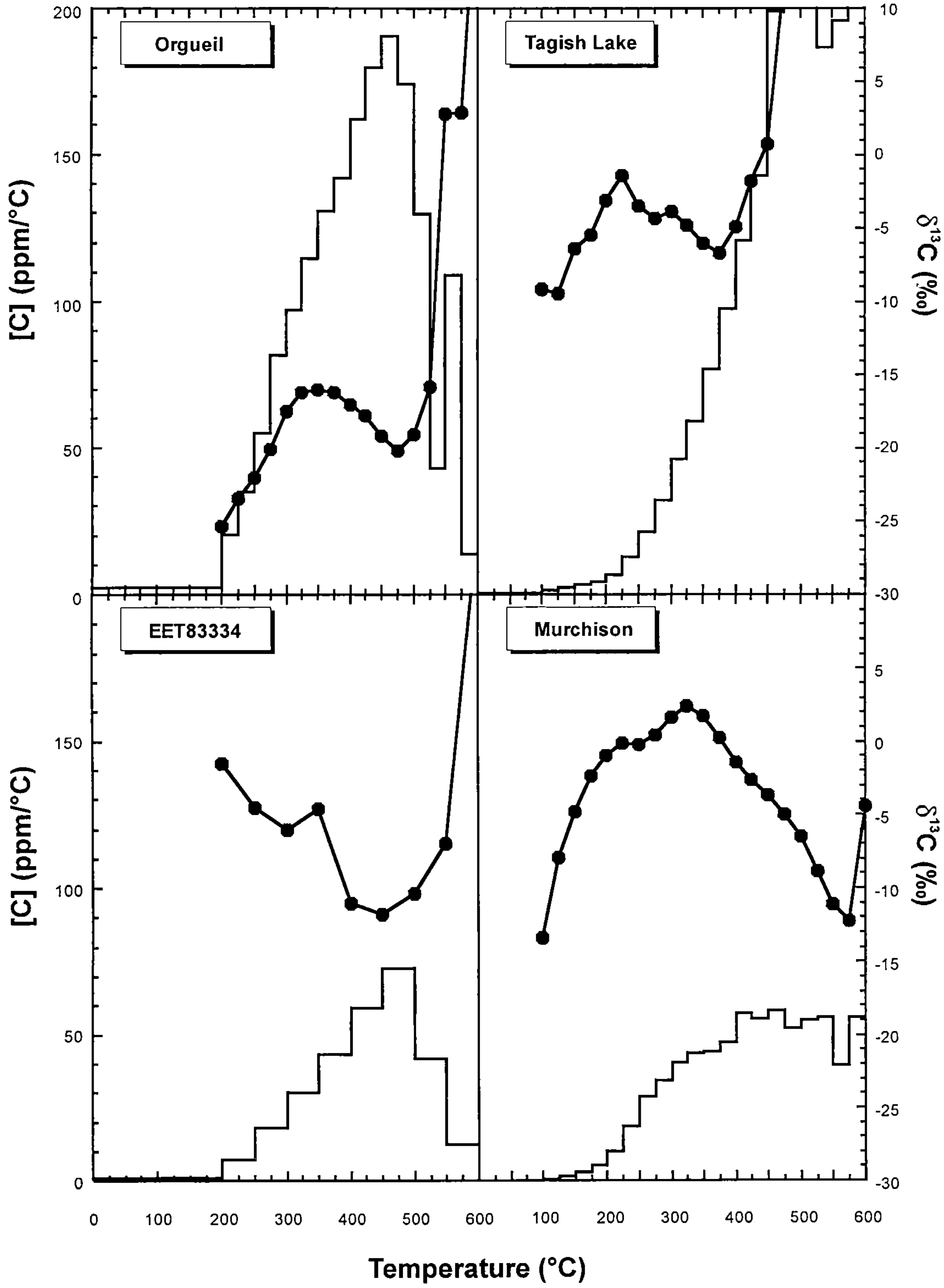

FIG. 4. Expanded view of low-temperature data given in Fig. 1 for carbon in CI and CM chondrites. Stepped combustion of (a) Orgueil, (b) Tagish Lake, (c) EET 83334 and (d) Murchison. The yield of carbon released at each step of the experiment (in ppm/°C) is given as a histogram; the corresponding isotopic composition is plotted as dots joined by a line. Errors in $\delta^{13}C$ are less than the size of the symbol.

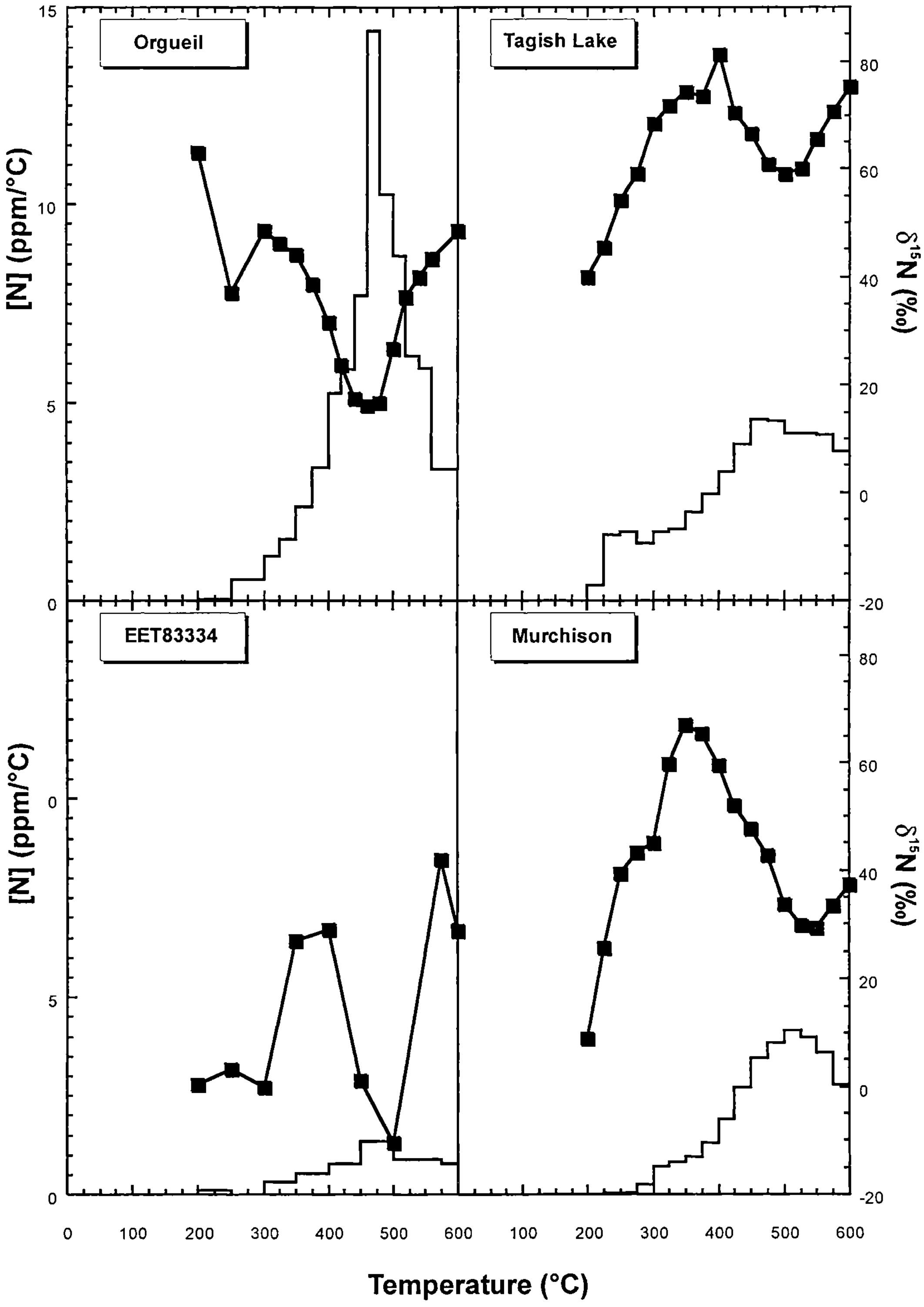

FIG. 5. Expanded view of low-temperature data given in Fig. 2 for nitrogen in CI and CM chondrites. Stepped combustion of (a) Orgueil, (b) Tagish Lake, (c) EET 83334 and (d) Murchison. The yield of nitrogen released at each step of the experiment (in ppm/°C) is given as a histogram; the corresponding isotopic composition is plotted as dots joined by a line. Errors in $\delta^{15}$N are less than the size of the symbol.

museums for Orgueil, and likely to be of the order of several hundreds of years in Antarctica for EET 83334). EET 83334 has the highest proportion of thermally labile nitrogen of all four chondrites studied, but its $\delta^{15}$N of +2‰ is consistent with identification as terrestrial nitrogen. Low-temperature organic material in Orgueil has a much lighter isotopic composition than the other meteorites, with $\delta^{13}$C down to –25‰. This is consistent with terrestrial contamination.

We can use the C/N ratio of the material combusting up to 225 °C to infer which organic species might be present in Tagish Lake. The model we use assumes that all the labile nitrogen arises from amino acids (the main nitrogen-bearing soluble organic species in Murchison) with C/N ratios of 2–5 (for the series of amino acids from glycine to valine). If that is the case, then approximately 20–50 ppm carbon is also from this source in Tagish Lake. We realise that the assumption is flawed, in that the $T < 225$ °C nitrogen in Tagish Lake has $\delta^{15}\mathrm{N} \approx +45$‰ (rather than the +90‰ of a pure amino acid fraction; Epstein *et al.*, 1987), and thus must in part comprise an unknown amount of nitrogen (with unknown $\delta^{15}$N) from combustion of side chain material. Thus the calculation represents an upper limit to the amount of carbon that can be ascribed to amino acids. Continuing on regardless, given that the calculated inventory of thermally labile organic species was equivalent to ~500 ppm carbon (Table 3), then approximately 450–480 ppm carbon comes from other solvent-soluble species, such as carboxylic acids, alkanes, *etc.* Pizzarello (2001) noted an apparent absence of carboxylic acids in Tagish Lake, but reported an abundance of dicarboxylic acids similar to that in Murchison (~5 ppm; Cronin *et al.*, 1993). Assuming $\delta^{13}$C of the acids is the same in Tagish Lake as in Murchison, at +45‰ for amino acids (Pizzarello *et al.*, 1991) and –6‰ for the dicarboxylic acids (Cronin *et al.*, 1993), then a mass balance calculation yields 445–475 ppm labile carbon with $\delta^{13}\mathrm{C} \approx -10$ to –6.5‰ for the remaining material. This is presumably the (mainly aliphatic) alkanes and alkenes described by Pizzarello (2001); the calculated $\delta^{13}$C fits well with observations for similar fractions in Murchison (*e.g.*, Becker and Epstein, 1982; Krishnamurthy *et al.*, 1992; Cronin *et al.*, 1993).

The less volatile macromolecular organic material combusts above 225 °C. Tagish Lake has a complement of macromolecular material and $\delta^{13}$C intermediate between Orgueil and Murchison. The C/N ratio of the total organic carbon in all three meteorites is remarkably constant (approximately 26–28), implying that its structure may be similar in the three parent objects. The higher C/N ratio (63) of organic carbon in EET 83334 presumably indicates that Antarctic weathering processes have modified the complex. In order to understand more readily data for the organic species, the residue following dissolution of whole-rock Tagish Lake in orthophosphoric acid was combusted. Results for carbon and nitrogen are shown in Fig. 6. Removal of the carbonates by $H_3PO_4$ has made more

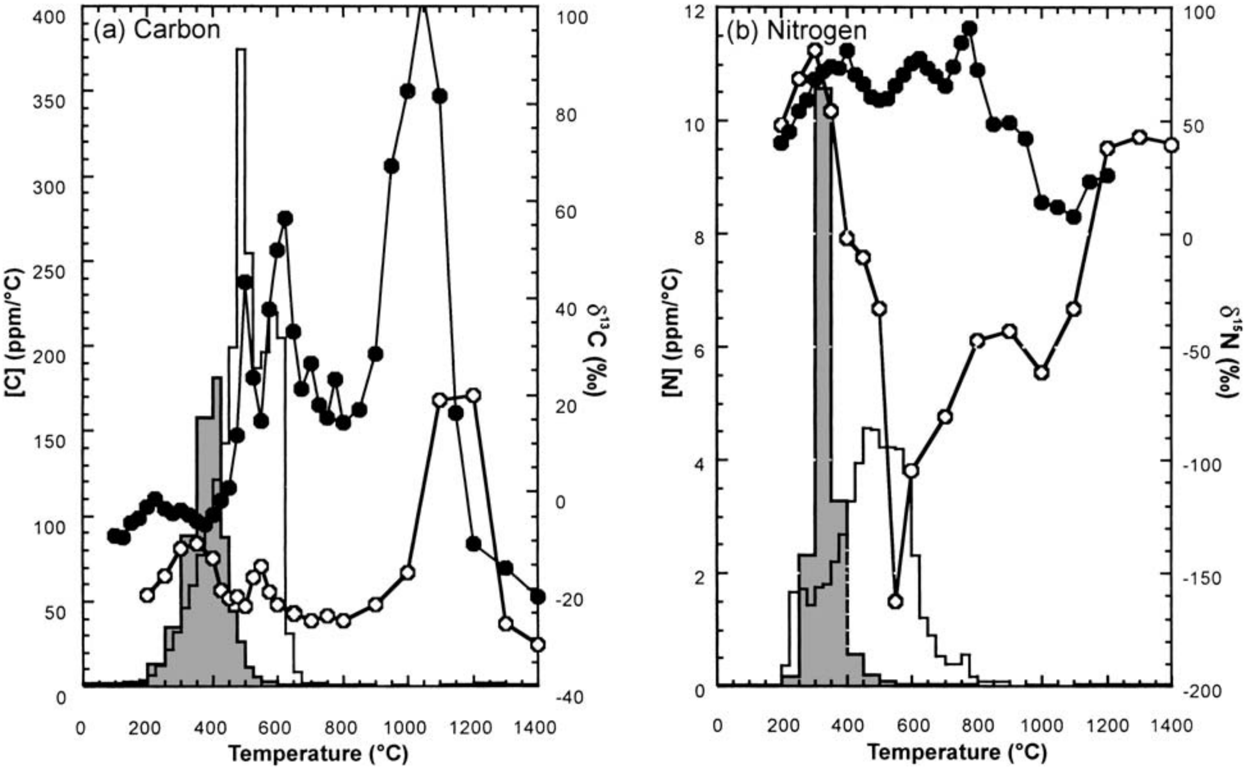

FIG. 6. Stepped combustion of an orthophosphoric acid-resistant residue (open symbols, shaded histogram) of Tagish Lake, normalised to and compared with data from the whole-rock parent (closed symbols, unshaded histogram). (a) Carbon; (b) nitrogen.

apparent, in carbon and nitrogen profiles, the combustion of interstellar nanodiamonds, depleted in both $^{13}$C and $^{15}$N (see later section). Since more than ~87% of the mass of the sample was lost on acid dissolution, it is clear that the acid attacked components (mainly silicates) in addition to carbonates. The treatment corresponded to a fairly vigorous acid hydrolysis (at temperatures up to 75 °C) of the macromolecular material.

Following acid treatment, the macromolecular material generally combusts at a lower temperature than in the whole rock—this applies to release of both carbon and nitrogen. The lower combustion temperature is either an effect of removing the mineral matrix, exposing the macromolecule, or acid treatment has hydrolysed sufficient bonds within the structure to cause the macromolecule to collapse. In either case, oxidation occurs more readily than in the undemineralised sample. The carbon isotopic compositions of the lowest temperature steps are no longer slightly elevated: $\delta^{13}$C is around –20‰, rising only to –17‰ at 250 °C. This is in contrast with the whole-rock data, where $\delta^{13}$C rises from –9‰ to reach a maximum of –1‰ at 225 °C. The change in $\delta^{13}$C might be a result either of addition of isotopically light terrestrial contaminants (with typical $\delta^{13}C \approx -25$‰) or loss of $^{13}$C-enriched soluble species. The low-temperature nitrogen isotopic composition remains almost unchanged between the whole-rock and acid-resistant residue, at around +50 to +80‰. If terrestrial contaminants had been added during production of the acid-resistant residue, then their effect would have been seen by a decrease in $\delta^{15}$N, since most terrestrial contaminants have $\delta^{15}$N close to 0‰. It seems, then, that the overall change in $\delta^{13}$C at low temperatures is a result of removal of organic components during dissolution. This confirms the interpretation that the material that combusts below 225 °C is also water- or acid-soluble.

A mass balance calculation for the amount of organic material removed by dissolution gives a total loss of ~5000 ppm carbon ($\delta^{13}$C between ~0 and +2‰) and ~189 ppm nitrogen ($\delta^{15}N \approx +162$‰), that is, ~20% of the total organic carbon and nitrogen. Given that only ~500 ppm carbon and ~12 ppm nitrogen combusted at low temperatures and thus were considered to be the most volatile of components and potentially solvent-extractable, then both carbon and nitrogen have been lost from the macromolecular component. Assuming 500 ppm carbon with $\delta^{13}C \approx -4.5$‰ and 12 ppm nitrogen with +44‰ have been lost as soluble organics (Table 3), then ~4500 ppm carbon with $\delta^{13}C \approx +1$ to +3‰ and ~180 ppm nitrogen with $\delta^{15}N \approx +170$‰ have been removed from the macromolecular component. This accounts for ~18% of the carbon and 20% of the nitrogen within the insoluble carbon, and is in reasonable agreement with the yields of acid-hydrolysable organic carbon measured by Becker and Epstein (1982) and calculated for Murchison (Pearson *et al.*, 2000) who found that hydrous pyrolysis removed a $^{13}$C- and $^{15}$N-enriched component.

The plot in Fig. 7 shows $\delta^{13}$C and yield for both the most thermally labile carbon and total organic carbon. Although it is probably unwise to draw too many conclusions from a graph with only three points, the plot shows that there is a regular relationship between Orgueil, Tagish Lake and Murchison in the two carbon reservoirs. CI and CM chondrites are assumed to be from separate parent bodies that experienced secondary aqueous processing at different temperatures and water–rock ratios (*e.g.*, Clayton and Mayeda, 1999). If that is the case, then from its organic chemistry alone Tagish Lake emanates from neither a CI nor a CM parent, but has affinities with both. However, recent models have been proposed that imply many mineralogical and geochemical characteristics could be explained by differential alteration of a single precursor (Young *et al.*, 1999; Bland *et al.*, 2000). If that were so, then Tagish Lake might simply be from an intermediate part of the spectrum between CI and CM.

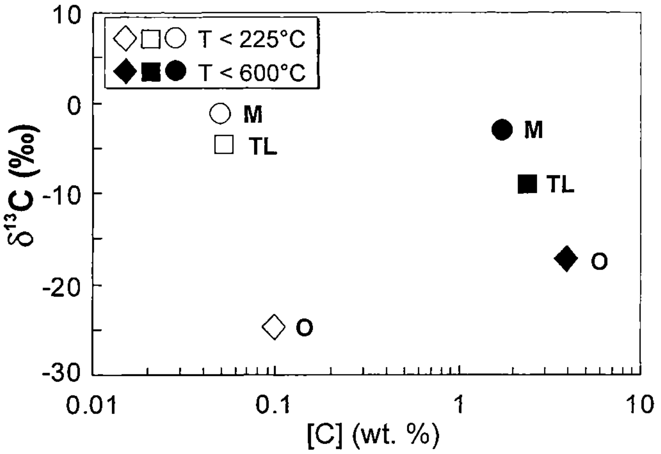

FIG. 7. Comparison of thermally labile carbon (open symbols) and total organic carbon (closed symbols) in Tagish Lake with Orgueil and Murchison.

The concentration of labile organic material increases from Murchison through Tagish Lake to Orgueil, its $\delta^{13}$C decreasing from –1 to –24‰. Given that the biggest hiatus is between Murchison/Tagish Lake and Orgueil, it is entirely possible (given its 138 years terrestrial history) that the results from Orgueil are influenced by additional terrestrial contaminants. An alternative interpretation, assuming that all the organics in Orgueil are pre-terrestrial, is that the coupled trends demonstrate that isotopically light carbon is synthesised or concentrated during aqueous processing, presumably as the more refractory aromatic core is degraded. Such an effect has already been described for different families of organic species within individual carbonaceous chondrites (*e.g.*, Sephton *et al.*, 1998, 2000). Isotopic analyses of the hydrous pyrolysates from Orgueil and Murchison led to the conclusion that the macromolecule was originally synthesised in the interstellar medium by gradual addition of $^{12}$C-rich molecules, and that its structure was subsequently modified by aqueous processing on asteroidal parents (Sephton *et al.*, 2000). If the CI, CM and Tagish Lake parent bodies began with inventories of similar organic species inherited from the presolar nebula and interstellar medium, even if present in different abundances (Alexander *et al.*, 1993), then parent-body processing has modified the species to different extents.

## CARBONATES

The abundance and isotopic composition of carbonates in Tagish Lake were measured by two methods: stepped combustion and acid dissolution. High-resolution stepped combustion of Tagish Lake (Fig. 1) shows that there are two maxima in the yield histogram, at 500 °C ($\delta^{13}C \approx +43‰$) and 600 °C ($\delta^{13}C \approx +56‰$). Pure carbonates with different end-member compositions decompose at different temperatures: siderite at approximately 400–450 °C, magnesite at approximately 525–575 °C and calcite at approximately 575–625 °C (Fig. 8); mixed carbonates, such as the Fe, Mg-carbonate breunnerite are assumed to break down at temperatures intermediate to those of the pure end-members. Thus, in Tagish Lake the lower temperature maximum is from decrepitation of Fe, Mg-carbonate, whilst the higher corresponds to decomposition of calcite (Table 4). Sequential acid dissolution of whole-rock Tagish Lake has allowed better distinction to be drawn between the different carbonates present. Within the error of the analysis, $\delta^{13}C$ is constant between the two carbonate types. Carbon isotopic values are higher than the equivalent compositions derived by stepped combustion, because of interference in the latter method from more $^{12}C$-enriched organic species and nanodiamonds. The initial report of carbonate abundance in Tagish Lake (Grady *et al.*, 2000), based on stepped combustion data alone, was an overestimate, as no allowance had been made for any contribution to the yield from co-combustion of other species.

Carbonate yield and carbon isotopic composition from acid dissolution is shown in Fig. 9a. The yield from stepped combustion (2.7 wt%) is twice that from acid dissolution (1.3 wt%), even though corrections have been applied to account for contributions to the yield from additional species such as organic material and nanodiamonds, which combust over the same temperature interval as that at which carbonates decrepitate. The stepped-combustion experiment was carried out on a ~1 mg fragment from Tagish Lake, whereas two separate aliquots, each ~30 mg were dissolved in orthophosphoric acid. Although care was taken to select a representative chip from Tagish Lake for combustion, it is likely that the high carbonate abundance from stepped combustion is a result of sample heterogeneity. In which case, the acid dissolution results are more likely to be a true measure of the overall carbonate abundance in Tagish Lake, although it is known that the acid also attacks, and thus releases $CO_2$ from, accompanying organic material. Petrographic studies have shown that although Fe, Mg- and Ca-carbonates occur throughout Tagish Lake, there are two lithologies, one of which is enriched in fine-grained carbonates relative to the other (Gounelle *et al.*, 2001); our carbonate results confirm the heterogeneous carbonate distribution. Even given the above caveats, between 1.3 and 2.7 wt% carbon derives from carbonates. This is a much higher proportion than is usual for either CI or CM chondrites, where typical carbonate abundances are 0.05–0.6 wt% carbon (Fig. 9a). The carbon isotopic composition of the Tagish Lake carbonate is, however, within the range of values for CI and CM chondrites, albeit at the most $^{13}C$-rich extreme (Grady *et al.*, 1988). The relative abundances of the two components indicate that Fe, Mg-carbonate (which is characteristic of CI chondrites) dominates over calcite (which is characteristic of CM chondrites) by approximately 4 to 1.

TABLE 4. Carbonates in Tagish Lake.

| Species* | Yield† (%) | $\delta^{13}C$‡ (‰) | $\delta^{18}O$ (‰) |
|---|---|---|---|
| **Stepped combustion (SC)** | | | |
| (1) 475–550 °C (Fe, Mg) | 1.41 | > +43 | – |
| (2) 575–625 °C (Ca, Mg) | 1.28 | > +56 | – |
| Total (SC) | 2.69 | – | – |
| **Acid dissolution (AD)** | | | |
| 25 °C (Ca) | | | |
| 28.770 mg | 0.23 | +68.1 | +31.7 |
| 29.051 mg | 0.24 | +66.7 | +32.1 |
| 75 °C (Fe, Mg) | | | |
| 28.770 mg | 1.05 | +66.9 | +34.7 |
| 29.051 mg | 1.05 | +68.3 | +36.4 |
| Total (AD) | | | |
| 28.770 mg | 1.28 | +67.1 | +34.2 |
| 29.051 mg | 1.29 | +68.0 | +35.6 |
| Mean (AD) | 1.285 | +67.6 | +35.2 |

*The order in which the carbonates are listed is reversed between the two methods. This is because Fe-Mg carbonates breakdown at a lower temperature than Ca carbonate, even though they are much more resistant to acid attack.

†Data for the yields of carbonate from stepped combustion are corrected for contributions from organic and presolar species. Details of the calculation are given in the appendix.

‡The tabulated $\delta^{13}C$ values are (1) the maximum values attained during stepped combustion and (2) the measured values from acid dissolution.

The oxygen isotopic composition of the carbonates (Fig. 9b) falls towards the high end of the range of values for CI and CM chondrites (Grady *et al.*, 1988; Benedix *et al.*, 2000). There is, however, a difference in $\delta^{18}O$ of ~4‰ between the calcite and dolomite/breunnerite (Table 4), with calcite having the lower $\delta^{18}O$. Such a pattern is consistent with the different carbonates forming from a single liquid with an isotopic composition that evolves through fluid–rock interaction, with calcite precipitating before dolomite or breunnerite (Riciputi *et al.*, 1994). This is in contrast to many other carbonaceous chondrites which have heavier calcite relative to their

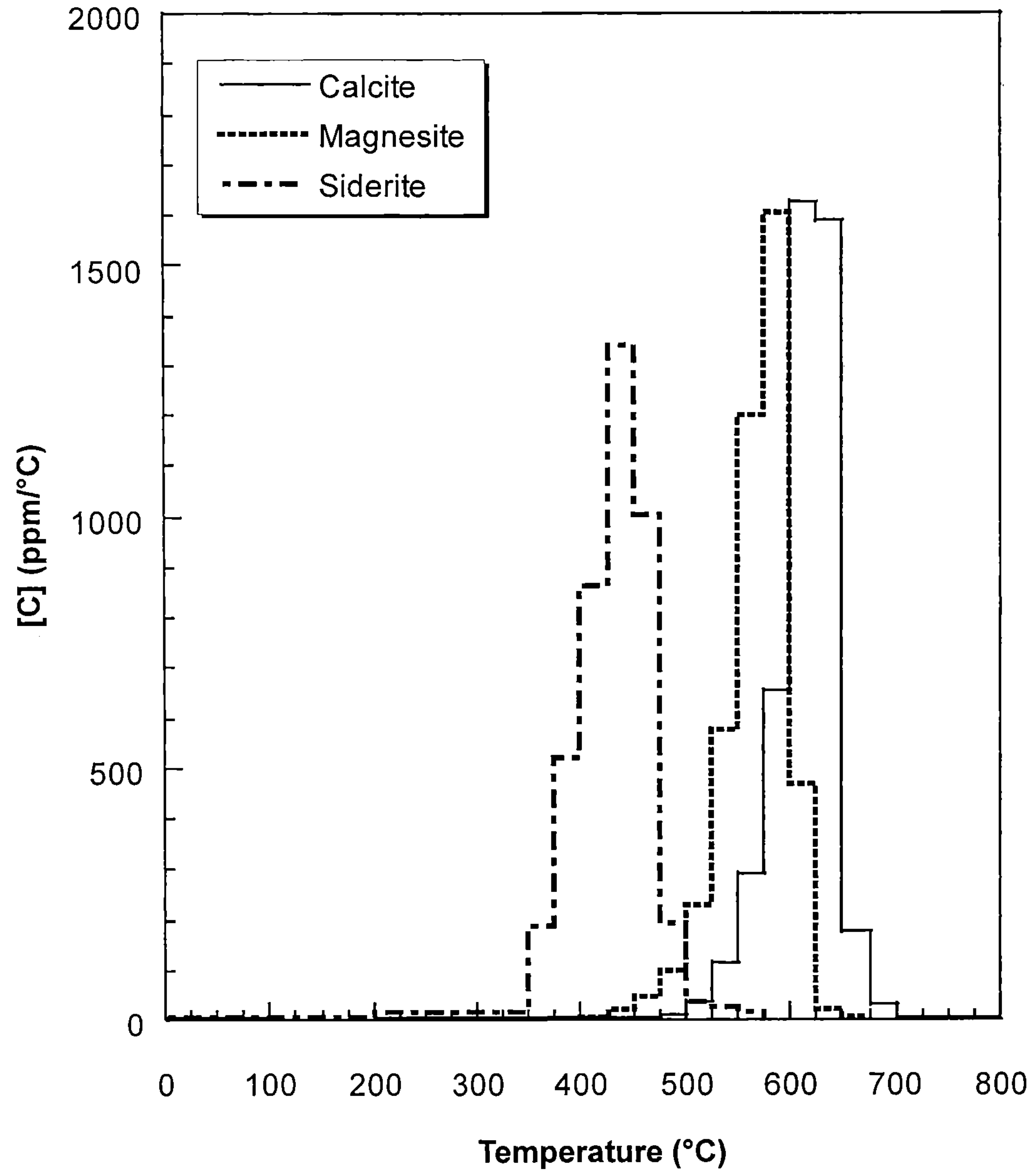

FIG. 8. Carbon yield from stepped combustion of three pure carbonate minerals. The temperature at which the maximum yield occurs varies with the chemical composition of the carbonates, such that $T_{max}$ increases in the order siderite ($FeCO_3$) < magnesite ($MgCO_3$) < calcite ($CaCO_3$). Comparison of data from high-resolution stepped combustion of meteorites containing mixed carbonates with these single compounds thus allows constraints to be placed on the mineralogical identification of carbonates in the meteorite, when the carbonates cannot be identified *in situ*.

corresponding dolomite/breunnerite (*e.g.*, Grady *et al.*, 1988; Leshin *et al.*, 2001). The considerable variation in $\Delta^{17}O$ of the different carbonate phases in Tagish Lake reported by Leshin *et al.* (2001) is also consistent with precipitation from an evolving fluid. Therefore $\delta^{18}O$ variation observed in the different carbonates in Tagish Lake must be the result of co-variation of the $\delta^{18}O$ value of the fluid phase, the temperature of the system and the chemical composition of the fluid.

There have been several detailed studies of the distribution and the major, minor and trace element chemistry of carbonates in CI and CM chondrites (*e.g.*, Zolensky and McSween, 1988; Johnson and Prinz, 1993; Riciputi *et al.*, 1994; Endress and Bischoff, 1996). Both Ivuna and Orgueil comprise distinct lithologies, one of which is very carbonate-rich (Endress and Bischoff, 1996); it has already been noted that carbonates are heterogeneously distributed in Tagish Lake, and that there is a fine-grained carbonate-rich lithology (Gounelle *et al.*, 2001). Similar lithologies have not been described in CM meteorites. On the basis of the distribution of cations between individual carbonate species in CI chondrites, inferences have been drawn concerning the composition of the fluid from which carbonates were precipitated (*e.g.*, Riciputi *et al.*, 1994). Most authors

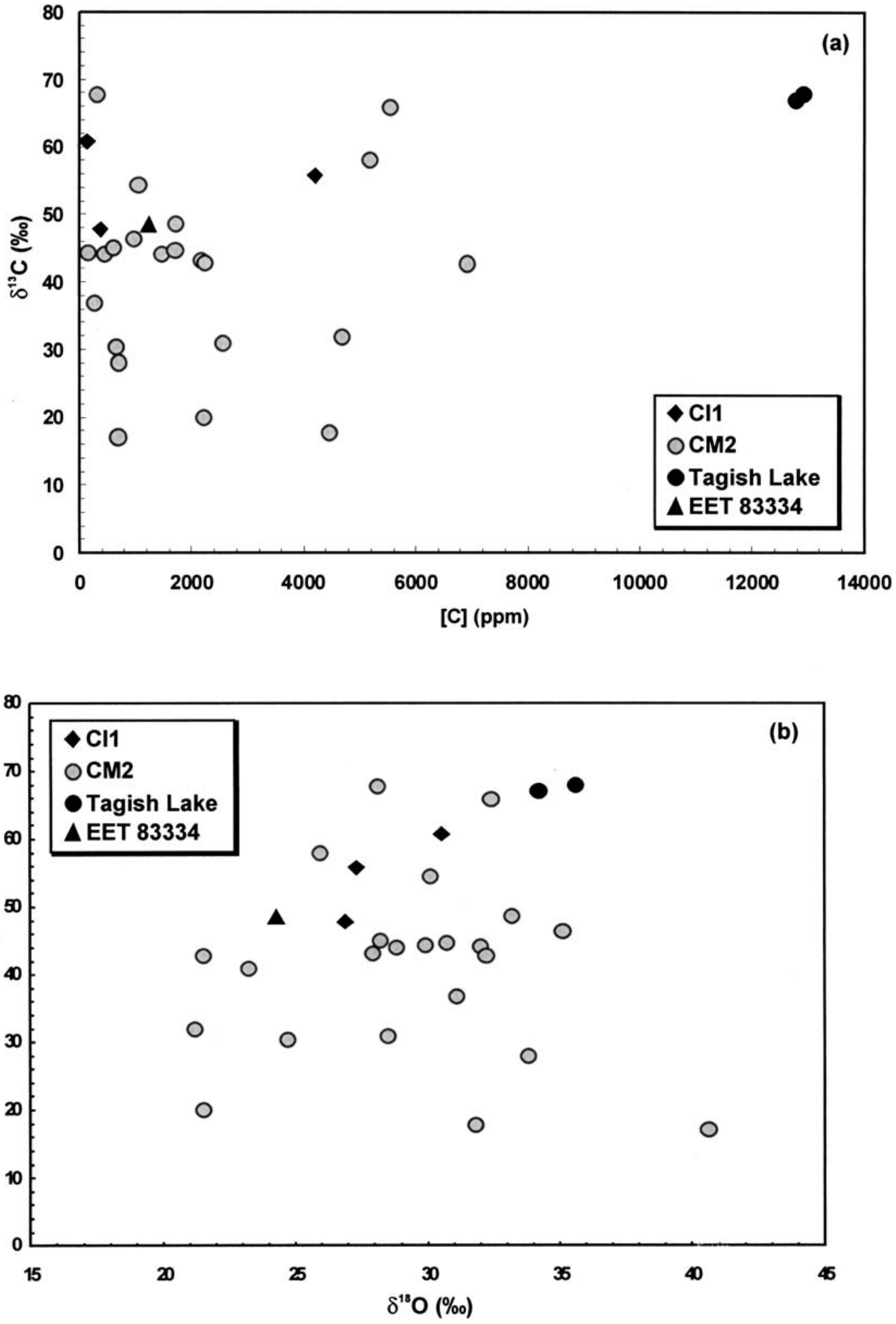

FIG. 9. Abundance and isotopic composition of carbonates in Tagish Lake (from orthophosphoric acid dissolution) compared with data from CI and CM chondrites (from Grady *et al.*, 1988).

agree that the carbonates were not in equilibrium with a single chemically homogeneous fluid that saturated the CI parent, but that individual carbonate grains were in local, closed-system, equilibrium with fluid. Changes in carbonate mineralogy, such as calcite to dolomite to breunnerite, indicate that the carbonates are not in mutual equilibrium. They therefore cannot have been deposited from an unchanging fluid, but result from distinct mineralising events as the fluid evolved, through dissolution of silicate minerals and/or changing temperature. Whilst there has not yet been an equivalent detailed study of carbonates in Tagish Lake, we can make some general observations on carbonate genesis based on the data to hand so far.

First of all, Tagish Lake exhibits the same range of carbonate elemental and isotopic compositions as CI chondrites; thus it is reasonable to infer that the formation mechanism was similar in the Tagish Lake and CI parent asteroids. Riciputi *et al.* (1994) outlined a method by which carbonates were produced from brines filtered through a clay membrane; they predicted that as the carbonate precipitated, the residual brine would become enriched in $^{18}$O. Late-stage carbonates in equilibrium with this evolved fluid would then have heavier oxygen isotopic compositions than the carbonates precipitated earlier. Using major element cation chemistry, Endress and Bischoff (1996) demonstrated that there was considerable variation in dolomite composition among CI chondrites, indicating that the CI parent was heterogeneous on local, as well as large, scales. By analogy with the precipitation of carbonate from terrestrial brines, Riciputi *et al.* (1994) suggested that Ca-rich carbonate precipitated before Mg- and Fe-rich end-members. If that were the case, then dolomite, precipitating after calcite, would have a heavier $\delta^{18}$O value. As shown in Table 4 (and confirmed by Leshin *et al.*, 2001), the results from Tagish Lake are in line with these predictions. The same result is found for Ivuna (Grady *et al.*, 1988), but the opposite trend appears to be the case for Orgueil (Leshin *et al.*, 2001), an indication that if Tagish Lake and the CI chondrites are all from the same parent body then carbonate paragenesis is indeed heterogeneous.

Although $\delta^{18}$O differs between the carbonate generations, $\delta^{13}$C is constant, approximately +67‰, implying a single source for carbon. If oxygen isotope variations in the fluid from which the carbonates precipitated result from localised reactions of the fluid with mineral grains, then the fluid must have become homogeneous in carbon, and then isolated from the carbon source, prior to carbonate precipitation. The carbon source is, as yet, unknown. Oxidation of fragments from the organic component could produce the feedstock for dissolved $CO_2$. However, the highest $\delta^{13}$C value recorded for any organic species is approximately +45‰ for amino acids (Pizzarello *et al.*, 1991), a value insufficiently enriched in $^{13}$C to be a viable source material. However, organics cannot be ruled out totally. If a significant fraction of the macromolecular material is interstellar, then there might be an isotopically heavier component within it that has not yet been identified. Or the putative $^{13}$C-rich entity might have been completely solubilised during parent-body alteration, leaving no trace (though this somewhat *ad hoc* explanation is perhaps unlikely). One other reservoir of $^{13}$C in CI and CM chondrites is that of $^{13}$C-enriched presolar grains, specifically graphite and silicon carbide (see below). These grains are resistant to acid and solvent attack (indeed, that is how they are isolated from whole-rock meteorites). They are, however, degraded by thermal metamorphism (Huss, 1990; Alexander *et al.*, 1990; Russell *et al.*, 1992; Huss and Lewis, 1995). Further studies need to be undertaken to investigate how susceptible these grains are to etching by alkaline fluids, given that most models predict a high pH value for the alteration medium (*e.g.*, Browning and Bourcier, 1996; Rosenberg *et al.*, 2001). If carbonate production is a local process, then it would only take dissolution of a few parts per billion of a highly $^{13}$C-enriched graphite or silicon carbide grain ($\delta^{13}C \geq +1000‰$) to produce a fluid from which carbonates ($\delta^{13}C \leq +100‰$) might be precipitated.

Yet another mechanism for production of $^{13}$C-enriched carbonates could be that the isotopic difference observed between carbonates and organics in carbonaceous chondrites is a result of fractionation processes accompanying Fischer–Tropsch type (FTT) reactions (Lancet and Anders, 1970; Hayatsu and Anders, 1981). This once popular idea, that was an adjunct to an overall hypothesis of solar system formation from a cooling nebula gas of solar composition, has declined in importance following refinement of models of nebular dynamics. However, FTT is currently undergoing something of a renaissance (Ferrante *et al.,* 2000; Hill and Nuth, 2000), where its operation with more realistic catalysts and under generic astrophysical conditions puts it once more back into consideration. It should be said that the degree of isotopic fractionation observed during FTT reactions in the laboratory (75‰ at 375 K; Hayatsu and Anders, 1981) is only just adequate to explain the full range of $\delta^{13}$C values observed in meteoritic carbonates. In light of lingering doubts regarding the applicability of FTT synthesis within the solar nebula, perhaps it makes sense to evaluate the reaction as a parent-body process. Within the conceptual framework of Young *et al.* (1999) and Bland *et al.* (2000), as a carbonaceous parent body is heated above 273 K, fluid begins to flow from the inner regions to the outer, causing mineralogical changes and leaving a record in the oxygen isotope systematics. It is conceivable that the same process is responsible for the flow of gases such as CO and $H_2$ that react over catalytic materials to form $CO_2$, ultimately precipitating as $CO_3^{2-}$. Certainly, the conditions available within a primitive parent-body would be compatible with the operation of an FTT process (*e.g.*, Asinger, 1968) as long as primordial gases remain present.

## INTERSTELLAR GRAINS

Carbonaceous chondrites are known to contain parts per billion to parts per million amounts of grains derived from different astrophysical environments: circumstellar, interstellar, supernovae, *etc.* These presolar grains are predominantly diamond, graphite and silicon carbide, with lesser quantities of oxides and nitrides. When the grains are analysed by ion microprobe as size separates from demineralised residues, they exhibit extreme carbon, nitrogen, silicon and noble gas isotopic compositions, which distinguishes them from solar system materials. The presence of the grains can also be identified from stepped-combustion experiments on milligram quantities of whole-rock meteorites, by excursions in $\delta^{13}$C and $\delta^{15}$N from normal solar system values (*e.g.*, Swart *et al.*, 1983). It is clear from variations in isotopic composition in whole-rock Tagish Lake (Figs. 1 and 2) that presolar grains occur within the meteorite. Since the identities, thermal combustion profiles, inventories and isotopic compositions of the most prevalent presolar grains are now reasonably well constrained (*e.g.*, Anders and Zinner, 1993; Zinner, 1997, 1998), it is possible to calculate "exotic" grain abundances from whole-rock data. And so, in this pathfinder study of Tagish Lake, we use known presolar grain compositions from CI and CM chondrites to infer a presolar grain inventory for Tagish Lake, prior to preparation of a suite of acid-resistant separates for more detailed analysis. Nanodiamonds (combusting at 500–550 °C), graphite (combusting at approximately 750–850 °C) and silicon carbide (combusting above ~900 °C) all appear to be present in Tagish Lake.

### Nanodiamonds (Temperature Approximately 500–550 °C)

Nanodiamonds are the most abundant of the presolar grains found in meteorites, present in concentrations of several hundred parts per million in CI1 and CM2 chondrites (*e.g.*, Huss, 1990; Huss and Lewis, 1995; Russell *et al.*, 1991, 1996). Nitrogen is a significant trace element within nanodiamonds, and they are also the host of the noble gas component Xe (HL). Although their precise origin is not fully understood, as the isotopic systematics of Xe (HL) are complex, presolar nanodiamonds are presumed to have formed by chemical vapour deposition in the expanding shell of a type II supernova (Clayton *et al.*, 1995). Individual crystallites of extra-solar diamonds are only ~3 nm across, thus isotopic measurement of discrete grains is not yet possible (and may never be possible), even with the most sensitive of techniques. Most analyses of interstellar nanodiamonds have been undertaken by combustion of diamond-rich fractions from acid-resistant residues. There appear to be several populations of nanodiamonds, not all of which might contain the unusual nitrogen or xenon (Russell *et al.*, 1991; Huss and Lewis, 1994, 1995; Verchovsky *et al.*, 1998). Nitrogen isotopic composition is a more diagnostic indicator for nanodiamonds than carbon: in their purest form, interstellar nanodiamonds have $\delta^{13}\text{C} \approx -38‰$, within the range of solar compositions, whereas $\delta^{15}$N falls as low as –348‰ (Russell *et al.*, 1996). Thus the presence of nanodiamonds in Tagish Lake can be inferred from the steep drop in $\delta^{15}$N around 500 °C, where $^{14}$N-enriched nitrogen is released as the nanodiamonds combust. Similar dramatic changes in $\delta^{15}$N are seen during stepped combustion of whole-rock Orgueil, Murchison and EET 83334 (Fig. 2), where $\delta^{15}$N drops by ~35‰. The effect of the presence of nanodiamonds on isotopic composition is more pronounced in the orthophosphoric acid-resistant residue of Tagish Lake (Fig. 6), where interference from organic carbon is reduced (the latter combusts at a lower temperature once the silicate matrix is removed, whereas nanodiamond combustion temperature remains almost unchanged).

From the carbon data, and knowing $\delta^{13}$C of the nanodiamonds, organic materials and carbonate end-members, it is possible to calculate an approximate abundance of interstellar nanodiamonds in Orgueil, EET 83334 and Murchison (Table 5 and appendix). The concentrations match well with determinations made from acid-resistant residues (Russell *et al.*, 1996), and inferred from noble gas concentrations (Huss, 1990; Huss and Lewis, 1995). The nanodiamond content of Tagish Lake (calculated for the orthophosphoric acid-resistant residue, and assumed to be the same in the whole rock) is much higher than the CI1 and CM chondrites. Although the final nanodiamond abundance is dependent on the end-member compositions selected for the deconvolution calculation, even the most extreme end-member composition yields a nanodiamond abundance higher than in any other chondrite (see appendix).

Modelling nitrogen release from the meteorites in terms of mixing between organic species and nanodiamonds gives nitrogen concentrations for the nanodiamonds. Again, these values match well with results from pure nanodiamond separates: Russell *et al.* (1996) determined the nitrogen concentration of nanodiamonds to be approximately 8500 ± 1100 ppm for CI1 and CM chondrites, compared with the values of approximately 5000–9000 ppm given in Table 5. However, the nitrogen concentration of nanodiamond in Tagish Lake is lower (*i.e.*, C/N ratio higher) than in the other chondrites, implying that nitrogen might have been lost from the nanodiamonds in Tagish Lake. Huss and Lewis (1994, 1995), considering noble gas contents, and Russell *et al.* (1996) considering nitrogen, ascribed the differing gas concentrations of higher petrologic type carbonaceous and ordinary chondrites to preferential destruction of gas-rich grains during thermal metamorphism. This secondary, parent-body, effect is probably not applicable to Tagish Lake, since it does not appear to have suffered thermal metamorphism. If there are several populations of nanodiamonds, it is possible that Tagish Lake contains a higher proportion of gas-poor grains, a primary effect of nebular heterogeneity. However, until complementary xenon analyses can be undertaken on Tagish Lake, we are not able to determine whether the difference in nanodiamonds between Tagish Lake and the other carbonaceous chondrites is a primary or a secondary effect, or simply a reflection that the abundance of nanodiamonds has been overestimated.

TABLE 5. Presolar grains in carbonaceous chondrites.

| | | Nanodiamonds* (450 °C < *T* < 550 °C) | | | | SiC† (*T* > 900 °C) | | | Diamond /SiC |
|---|---|---|---|---|---|---|---|---|---|
| | | [C] (ppm) | [N]‡ (ppm) | [N]§ (ppm) | C/N (at) | [C] (ppm) | [N] (ppb) | C/N (at) | |
| Orgueil | CI1 | 1634 | 13 | 7956 | 147 | 8.1 | 221 | 43 | 202 |
| Tagish Lake# | CI2 | 3646–4327 | 20 | 4622–5485 | 213–252 | 8.0 | 45 | 207 | 456–541 |
| TL residue#,$ | CI2 | 3646–4327 | 21 | 4853–5760 | 203–240 | 5.3 | 290 | 21 | 688–816 |
| EET 83334 | CM1 | 856 | 7.5 | 8761 | 133 | 4.8 | 47 | 119 | 178 |
| Murchison | CM2 | 492 | 3.5 | 7114 | 164 | 5.3 | 83 | 75 | 93 |

*The abundances were calculated assuming $\delta^{13}C = -38$‰ and $\delta^{15}N = -348$‰ for the nanodiamonds (Russell *et al.*, 1996). Full details of the calculation are given in the appendix.

†Calculated assuming $\delta^{13}C = +1430$‰ and $\delta^{15}N = -500$‰ (Amari *et al.*, 2000; Hoppe *et al.*, 1994; Russell *et al.*, 1997), see appendix. Nitrogen abundances are upper limits, as no allowance has been made for the presence of silicon nitride. The C/N ratio is therefore a lower limit.

‡Concentration of nitrogen from nanodiamonds relative to whole rock.

§Concentration of nitrogen in nanodiamond.

#For Tagish Lake, the abundance of nanodiamonds is calculated for the residue, and assumed to be the same in the whole rock-sample (see appendix).

$Residue from orthophosphoric acid dissolution; figures corrected for 87% weight loss on dissolution, and quoted relative to whole-rock values.

### Graphite (Temperature Approximately 800 °C)

Graphite combusts at ~800 °C, its actual combustion temperature varying with degree of crystallinity. Presolar graphite grains comprise ~2 ppm of CM2 chondrites (Anders and Zinner, 1993); most studies of the grains have been by ion microprobe analysis of density fractions from acid-resistant residues of Murchison (Hoppe *et al.*, 1995; Zinner *et al.*, 1995). Transmission electron microscopy and Raman spectroscopy of presolar graphite show that it exhibits a range of crystallinities, from poorly-graphitised carbon to well-crystalline graphite (Bernatowicz *et al.*, 1991; Zinner *et al.*, 1995). The precise origins of presolar graphite are the least well understood of all "exotic" grains. The graphite exhibits a variety of morphologies and a wide range in carbon and nitrogen isotopic compositions (Hoppe *et al.*, 1995; Zinner *et al.*, 1995; Travaglio *et al.*, 1999). $^{12}C/^{13}C$ ranges from 7 to 4500 ($\delta^{13}C \approx -980$‰ to +12 000‰) whilst $^{14}N/^{15}N$ ranges from 28 to 680 ($\delta^{15}N \approx -600$‰ to +9000‰). Isotopic composition varies according to the density of the acid-resistant fraction analysed. The carrier of Ne-E (L), a noble gas component produced in novae, was identified as graphite (Amari *et al.*, 1990). The gas-rich grains only comprise a small percentage (<1%) of the graphite (Kehm *et al.*, 1996), and at least four groups of presolar graphite have since been isolated, presumably with four separate origins. Possible origins for different groups of graphite include an ONe novae explosion (*i.e.*, those rich in oxygen and neon) (Amari *et al.*, 2001), He-burning in Wolf–Rayet stars or type II supernovae (Anders and Zinner, 1993; Hoppe *et al.*, 1995). Given such a range of possible environments in which graphite can be produced, it is perhaps not surprising that there is no well-defined preferred $\delta^{13}C$ or $\delta^{15}N$ value, as there is for silicon carbide (SiC) (see below). There is a slight preponderance of graphite grains with $^{12}C/^{13}C \approx 10$–80 and slightly elevated $\delta^{15}N$ (Hoppe *et al.*, 1995). However, because there is no dominant $\delta^{13}C$ or $\delta^{15}N$ value, it is not possible to calculate approximate graphite concentrations for Tagish Lake or the other carbonaceous chondrites from whole-rock stepped combustion data. All that may be inferred from the data is that presolar graphite seems to be present in Tagish Lake, as shown by a sharp increase in $\delta^{15}N$ at 750–800 °C, accompanied by a slight drop in $\delta^{13}C$. Given that its $\delta^{15}N$ reaches +90‰ at 775 °C ($^{14}N/^{15}N \approx 250$), a higher value than in any of the other three chondrites considered, it is possible that Tagish Lake is richer in presolar graphite than the other chondrites.

### Silicon Carbide (Temperature Greater Than 950 °C)

Silicon carbide combusts above 950 °C. Ion microprobe analyses of micron-sized separates from acid-resistant residues of carbonaceous chondrites show that SiC grains have a very wide range of carbon, nitrogen and silicon isotopic compositions (Virag *et al.*, 1992; Hoppe *et al.*, 1993, 1994, 1996; Huss *et al.*, 1997). Their isotopic characteristics indicate that meteoritic SiC grains have emanated from several different astrophysical environments, including low-mass AGB stars, J- and R-type carbon stars and ejecta from type II supernovae (*e.g.*, Alexander, 1993; Anders and Zinner, 1993; Hoppe *et al.*, 1996; Zinner, 1997, 1998). However, most SiC grains (~90% of the total) belong to a single population, and are enriched in $^{13}C$ and depleted in $^{15}N$ (Amari *et al.*, 2000; Hoppe *et al.*, 1994, 1996; Huss *et al.*, 1997). Such "mainstream" SiC grains are assumed to be synthesised in an expanding envelope around thermally pulsing low-mass AGB stars (*e.g.*, Anders and Zinner, 1993; Hoppe *et al.*, 1996). Elevated $\delta^{13}C$ and depressed $\delta^{15}N$ are characteristics exhibited by material combusting above 950 °C in Orgueil and Murchison, although the most extreme isotopic compositions measured in whole-rock meteorites are subdued compared with values from separated grains. Thus $\delta^{13}C$ reaches +220‰ in Orgueil, and +130‰ in Murchison, whilst $\delta^{15}N$ drops to +10‰ in Orgueil and –5‰ in Murchison. Tagish Lake also demonstrates these variations in isotopic composition, with $\delta^{13}C$ reaching a maximum of +105‰ and $\delta^{15}N$ dropping down to +5‰. Yields of carbon and nitrogen at these temperatures are low, but still higher than blank levels.

The extreme compositions of the SiC grains are presumably diluted by simultaneous combustion of material with a more normal isotopic composition. Assuming mixing between SiC ($\delta^{13}C \approx +1430$‰; $\delta^{15}N \approx -500$‰) and system background ($\delta^{13}C \approx -25$‰; $\delta^{15}N \approx +20$‰), abundances for whole-rock Orgueil, Tagish Lake, EET 83334 and Murchison are between 5 and 8 ppm (Table 5). These results are in reasonable agreement with the abundances calculated from demineralised residues (Huss, 1990; Amari *et al.*, 1994). Although we can assume that the bulk of the carbon combusting above 950 °C is from SiC, the same assumption cannot be made for nitrogen, since minor amounts of nierite ($Si_3N_4$) might also be present. Thus the nitrogen abundances given for SiC in Table 5 are upper limits, and include an unknown contribution from presolar nitrides. The $H_3PO_4$-resistant residue from Tagish Lake seems to have a lower SiC content than the whole-rock material. We can speculate that some grains might have been destroyed by the oxidising acid treatment, leading to an observation that not all the $^{13}C$-enriched $CO_2$ released by acid hydrolysis was from dissolution of carbonates. Alternatively, it might simply be a reflection of sample heterogeneity.

What can be seen from the data in Table 5 is that the nanodiamond/SiC ratio of Tagish Lake is much higher than that of the other chondrites. As discussed above, this is a consequence of an enhanced nanodiamond abundance in Tagish Lake, rather than a depletion in SiC. Huss and Lewis (1995) suggested that CI and CM chondrites had inherited similar nanodiamond to SiC ratios from the presolar nebula, and that any differences were a result of secondary parent-body processes. So, has Tagish Lake lost SiC during parent-body alteration? Again, we return to the possibility considered in the carbonate section, that $^{13}C$-enriched SiC grains might have been destroyed during hydrous processing on the Tagish Lake parent, rather than by thermal metamorphism. Huss and Lewis showed that in carbonaceous chondrites diamond was more stable (*i.e.*, less susceptible to thermal metamorphism than SiC). Russell *et al.* (1996) observed that nanodiamonds in relatively unaltered chondrites had higher nitrogen abundances than those in more metamorphosed chondrites. They concluded that preferential destruction of gas-rich nanodiamonds during thermal metamorphism, rather than a single diamond degassing event, was responsible for the differences in nanodiamond nitrogen abundance. We can relate the observations of Huss and Lewis (1995) and Russell *et al.* (1996) to presolar grains in Tagish Lake. Tagish Lake seems to have a high nanodiamond abundance, but the nanodiamonds are depleted in nitrogen, implying destruction of gas-rich grains by thermal processing. Tagish Lake has a high nanodiamond to SiC ratio, implying that SiC has been destroyed, presumably by the same processes that destroyed gas-rich diamonds. The validity, or otherwise, of this conclusion, will be tested when noble gas data have been acquired for presolar grains from Tagish Lake.

## SUMMARY

The parent asteroids of CI and CM carbonaceous chondrites are known to have experienced extensive hydrothermal alteration, across a variety of regimes. Different parameters have been used to infer the different asteroidal environments. Most information comes from the oxygen isotopic composition of co-existing carbonates, anhydrous and hydrated silicates within carbonaceous chondrites. Modelling of oxygen isotopic compositions show that the CI parent was a warmer and wetter environment than the CM parent (*e.g.*, Clayton and Mayeda, 1999). Extension of the Clayton and Mayeda (1999) model to oxygen isotope data from Tagish Lake suggested that the meteorite was from a CI-like body, but had experienced alteration at lower temperatures (Brown *et al.*, 2000; Clayton and Mayeda, 2001). Petrologic and mineralogical studies have shown that Tagish Lake does not fit comfortably into either a CI or CM classification (Brown *et al.*, 2000; Zolensky *et al.*, 2000), thus it has been classified as the first, and so far only, CI2 chondrite. We conclude that the carbon and nitrogen isotope geochemistry of Tagish Lake is consistent with this classification. There are sufficient similarities between Tagish Lake and CI and CM chondrites to allow the light element geochemistry of Tagish Lake to be interpreted within the framework of results from CI and CM chondrites.

The inventory of organic carbon in Tagish Lake supports its classification as a CI2. It has a total organic carbon content (~2.5 wt%) intermediate between Orgueil and Murchison, and although the organic carbon has a similar core structure to Murchison, as described by its atomic C/N ratio, a lower overall percentage of it is soluble. This implies either that a proportion of the soluble organics has been lost, or, if soluble organics are produced by pre-terrestrial aqueous processing, were simply not made on the Tagish Lake parent. It is possible that this could have been a result of the short (but icy) terrestrial history of Tagish Lake. The samples analysed were of the "pristine" material that remained frozen from the time of the meteorite's fall until its sampling for analysis, so it is more attractive to consider the lower volatile content to be a result of parent-body processes. Because the remaining organic material is nitrogen-rich, it is inferred that parent-body processes have removed a nitrogen-poor component such as carboxylic acids.

Carbonate mineralogy, combined with their carbon and oxygen isotopic compositions, suggests that the carbonates in Tagish Lake were precipitated from a cooling fluid percolating through a CI-like substrate. The enhanced carbonate abundance, and carbonate distribution shows that the amount of alteration was substantial, but heterogeneous, and may have been localised in enclosed regions of the Tagish Lake parent.

Tagish Lake has a primordial ancestry that relates it to CI chondrites. It contains abundant presolar nanodiamonds and SiC, but differences in the presolar grain inventory between Tagish Lake and other carbonaceous chondrites suggest that processing might have destroyed a proportion of the SiC, along with a gas-rich fraction of the nanodiamonds.

The Tagish Lake meteorite is a carbonaceous chondrite that clearly has affinities to both CI and CM chondrites. On the basis of its carbon systematics, Tagish Lake has more similarities with CI than CM chondrites. However, there are sufficient differences in its mineralogy, petrology and geochemistry to suggest that it has not experienced exactly the same asteroidal weathering history as the CI parent. The primitive nature of Tagish Lake has the potential to yield important information on organic material inherited from interstellar clouds and processed through asteroidal parent bodies. This broad-brush study of carbon and nitrogen in Tagish Lake, intended as a pathfinder for more specialist studies, has shown that Tagish Lake is one of the most carbon-rich of chondrites, and is well endowed with presolar grains (nanodiamonds, graphite and silicon carbide).

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# APPENDIX

## Deconvolution of Carbon-Bearing Components in Tagish Lake

A very simple mixing model is used to calculate the end-member abundance and overall isotopic composition of organic carbon. The steps used in the calculations are:

(1) Material combusting below ~375 °C is not affected by interference from other species, and is considered to be organic material alone. This accounts for ~6683 ppm carbon with $\delta^{13}C \approx -5.4‰$.

(2) The regular decline in $\delta^{13}C$ with temperature (as shown in the seven consecutive temperature increments between 225 and 375 °C, Table 1) is extrapolated to 500 °C, predicting a gradual decrease in $\delta^{13}C$ of the organic complex from –1.4‰ at 225 °C to –7.8‰ at 400 °C and –12‰ at 500 °C. This is consistent with measurement of the insoluble organic material in the orthophosphoric acid-resistant residue (Table 1), and also with data for macromolecular material in CI and CM chondrites (*e.g.*, Cronin and Chang, 1993).

(3) Between 400 and 500 °C, carbon is also released from the decomposition of carbonate. Results from acid dissolution experiments show that the carbonate has a $\delta^{13}C$ of +67‰ (Table 4). Carbonate carbon is mixed with a contribution from organic species with $\delta^{13}C$ declining from –8‰ to –12‰ (from step (2), above). It is calculated that over this temperature range, a total of 14 221 ppm organic carbon with overall $\delta^{13}C \approx -9.8‰$ combusts.

(4) Between 500 and 600 °C, as well as carbon from carbonate and organics, there is a contribution from combustion of presolar nanodiamonds. It is necessary to know the nanodiamond content of Tagish Lake before the final abundance of organic matter can be calculated. Upper and lower limits for the abundance of presolar nanodiamonds in Tagish Lake were determined from analysis of an orthophosphoric acid-resistant residue, from which all carbonate had been removed. The nanodiamond abundance limits were calculated by assuming that carbon in the residue combusting between 400 and 600 °C came solely from a mixture of nanodiamonds and organics. Based on data from other carbonaceous chondrites, nanodiamonds have a $\delta^{13}C \approx -38‰$ (Russell *et al.*, 1996). The range of nanodiamond contents came from the assumed $\delta^{13}C$ of the organic matter. End-member isotopic compositions of $\delta^{13}C = -10.6‰$ and –12.0‰ were selected for the organic matter. The former value is the maximum $\delta^{13}C$ of the organic carbon in the Tagish Lake residue, whilst the latter is the total $\delta^{13}C$ of the $T < 400$ °C steps in the acid-resistant residue, the steps in which the organic carbon is probably not affected by co-combustion of nanodiamonds (Table 1). These end-member compositions are similar to the $\delta^{13}C$ values extrapolated from whole-rock data (steps (2) and (3) above). Using $\delta^{13}C$ of –12.0‰ and –10.6‰ as end-member compositions for organic carbon gives nanodiamond abundances of ~3646 and ~4327 ppm. Even the lower limit is higher than that calculated for any other carbonaceous chondrite (Russell *et al.*, 1996).

(5) Upper and lower limits for the amount of organic carbon combusting ($A_o$; and the amount of carbonate decrepitating, $A_c$) between 500 and 600 °C in whole-rock Tagish Lake is then calculated using the following parameters:

Total carbon (500–600 °C): 21 433 ppm ($A_t$);
$\delta^{13}C = +31.5‰$ ($\delta_t$) (Table 1)

Upper limit:
  Nanodiamonds: 3646 ppm ($A_d$); $\delta^{13}C = -38‰$ ($\delta_d$)
  Carbonate: $\delta^{13}C = +67‰$ ($\delta_c$)
  Organics: $\delta^{13}C = -12.0‰$ ($\delta_o$)

Lower limit:
  Nanodiamonds: 4327 ppm; $\delta^{13}C = -38‰$
  Carbonate: $\delta^{13}C = +67‰$
  Organics: $\delta^{13}C = -10.6‰$

$A_t = A_d + A_c + A_o$

$A_t\delta_t = A_d\delta_d + A_c\delta_c + A_o\delta_o$

Amount of organic carbon =

$$A_t - A_d + \{A_t\delta_t - A_d\delta_d - (A_t - A_d)\delta_o\}/(\delta_o - \delta_c)$$

The calculation indicates a lower limit of ~3953 ppm and an upper limit of ~4788 ppm organic carbon combusting between 500 and 600 °C, depending on the assumed nanodiamond abundance (which is, in turn, dependent on the assumed $\delta^{13}C$ of the organic component).

(6) The final abundance of organic carbon in whole-rock Tagish Lake is given by the sum of the quantities calculated in steps (1), (3) and (5):

| Temperature (°C) | [C] (ppm) | $\delta^{13}C$ (‰) |
|---|---|---|
| $T < 400$ | 6683 | -5.4 |
| 400–500 | 14 221 | -9.8 |
| 500–600 (a) | 3953 | -10.6 |
| 500–600 (b) | 4788 | -12.0 |
| Total (a) | 24 857 | -8.8 |
| Total (b) | 25 692 | -9.1 |

(7) It is appreciated that the calculation of nanodiamond abundance described in the preceding steps is critically dependent on the $\delta^{13}C$ value assumed for the isotopic composition of organic matter in the Tagish Lake acid-resistant residue. Justification for the values that have been used is given in step (4) above. We can, however, consider the effect of selecting more extreme $\delta^{13}C$ values for the organic matter. For $\delta^{13}C$ values heavier than -9‰ (the overall $\delta^{13}C$ of organic matter in whole-rock Tagish Lake), nanodiamond abundances exceed 5000 ppm, amounts much higher than seen in any other chondrite. In contrast, selecting a $\delta^{13}C \approx -15$‰ (the maximum $\delta^{13}C$ exhibited by the organic carbon plus nanodiamond mix in the residue), results in a nanodiamond abundance ~2300 ppm, a value still well above those of other chondrites.

(8) A similar procedure was applied to data from Orgueil, Murchison and EET 83334, with the difference that the lower abundance of carbonates in these samples allowed direct calculation of the abundance of nanodiamonds, since there was no apparent overlap between carbon from combustion of nanodiamonds and from carbonate decomposition. Data were treated as the sum of "uncompromised" organic material (combusting at about $T < 400$ °C) with simple mixtures between nanodiamonds and organics (approximately 400–550 °C) and carbonate and organics (approximately 550–650 °C). For each meteorite, the $\delta^{13}C$ of the organic component was extrapolated from the "uncompromised" material, as described in step (2) above. The $\delta^{13}C$ values used to model carbonate decomposition were from Grady *et al.* (1988) and Zolensky *et al.* (1997). The nanodiamond abundances calculated match well with data derived from analysis of more pure diamond separates (Russell *et al.*, 1996; Huss and Lewis, 1994).

(9) Determination of SiC abundances is also dependent on the end-member compositions selected. We assumed mixing between SiC and system background ($\delta^{13}C \approx -25$‰ and $\delta^{15}N \approx +20$‰). The isotopic composition of SiC was taken as $\delta^{13}C \approx +1430$‰ and $\delta^{15}N \approx -500$‰. These values are those obtained from stepped combustion of relatively pure SiC separates (Russell *et al.*, 1997) and from ion microprobe measurements of bulk "mainstream" SiC grains (Amari *et al.*, 2000). They are also similar to the mass-weighted averages determined by ion microprobe for individual SiC grains in the KJH (~4.5 $\mu$m) size separate from Murchison (Hoppe *et al.*, 1994).