

The oxygen isotopic composition of water from Tagish Lake: Its relationship to low-temperature phases and to other carbonaceous chondrites

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Abstract—The fall and recovery of the Tagish Lake meteorite in British Columbia in January 2000 provided a unique opportunity to study relatively pristine samples of carbonaceous chondrite material. Measurements of the oxygen isotopic composition of water extracted under stepped pyrolysis from a bulk sample of this meteorite have allowed us to make comparisons with similar data obtained from CI and CM chondrites and so further investigate any relationships that may exist between these meteorites. The much lower yield of water bearing a terrestrial signature in Tagish Lake is indicative of the pristine nature of the meteorite. The relationship between the isotopic composition of this water and reported isotopic values for carbonates, bulk matrix and whole rock have been used to infer the extent and conditions under which parent-body aqueous alteration occurred. In Tagish Lake the difference in $\Delta^{17}\text{O}$ isotopic composition between the water and other phases is greater than that found in either CM or CI chondrites suggesting that reaction and isotopic exchange between components was more limited. This in turn suggests that in the case of Tagish Lake conditions during the processes of aqueous alteration on the parent body, which ultimately controlled the formation of new minerals, were distinct from those on both CI and CM parent bodies.

INTRODUCTION

Elucidating the processes that have occurred on primitive meteorite parent bodies and understanding the relationship between different classes of primitive meteorites has been dominated in recent years by research into the processes of low-temperature alteration (*e.g.*, Clayton and Mayeda, 1984; Zolensky *et al.*, 1993; Browning *et al.*, 1996; Young *et al.*, 1999). By their very nature, low-temperature alteration products in meteorites are largely similar to those found in terrestrial samples. Therefore, Tagish Lake offers a unique opportunity to study rare carbonaceous chondrite material with limited terrestrial effects and could provide new data on early solar system oxygen reservoirs and the extent to which solid and fluid components may have interacted on parent bodies. Simultaneously it may help elucidate the extent of reaction of hydrated minerals with terrestrial water and oxygen reservoirs after arrival. Preliminary studies (*e.g.*, Brown *et al.*, 2000; Gounelle *et al.*, 2001) identified the Tagish Lake meteorite as a type 2 carbonaceous chondrite but with more similarities to CI than to CM chondrites. Two distinct lithologies, a dominant carbonate-poor lithology and a less abundant carbonate-rich lithology have been identified (Gounelle *et al.*, 2001), each lithology seemingly possessing distinct isotopic values for separate constituents (*e.g.*, Clayton and Mayeda, 2001; Engstrand

et al., 2001; Leshin *et al.*, 2001). We have measured the oxygen isotopic composition of water extracted from pristine samples of Tagish Lake that had remained frozen since initial impact, using a recently developed stepped-pyrolysis/fluorination system. In addition to measuring isotopic values, the method allows us to identify water emanating from different reservoirs within the samples (*i.e.*, inter-layer, adsorbed or structural water depending upon the temperature of release). The resulting yield and isotopic data more closely resemble patterns derived from CI meteorites than those from CM samples.

ANALYTICAL TECHNIQUE

Measurements of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ were made on water released by pyrolysis of a crushed, bulk meteorite sample of 4.05 mg, using a continuous-flow, isotope ratio mass spectrometer (Delta C, Finnigan Mat). The sample analysed in this study was from a ~5 g piece of pristine material provided for analysis by Jim Brook, and prepared by Michael Zolensky and Andrew Steel. It was identified as being from the carbonate-poor lithology after the study of Grady *et al.* (2001) who, using a subsample from the same fragment as that used in this study, found carbonate yields and oxygen ($\delta^{18}\text{O}$) isotopic values similar to those found by Leshin *et al.* (2001) from a piece of the carbonate-poor lithology. The subsample used in

this study was separated from a larger piece while still frozen. It was then ground using a pestle and mortar and loaded into the purged extraction system within 1 h of warming to room temperature. Water evolved from the sample during pyrolysis was swept by a flow of purified helium directly onto the in-line fluorinating agent (CoF_3), releasing oxygen. Isotopic exchange between extracted water and system components was restricted by keeping the distance travelled to a minimum (~ 70 mm) so that only 1 or 2 s elapsed between extraction and conversion by the fluorinating agent. Unwanted reaction products, mainly HF, were removed from the flow by a trap of NaF backed up by a cryogenic trap. Oxygen was collected by cryo-focussing on a length of PLOT column containing 5 Å molecular sieve held at liquid nitrogen temperatures, before passage through a capillary gas chromatography column for purification and finally to the mass spectrometer for analysis. Samples were heated in a step-wise manner from room temperature to 800 °C, with steps of either 33 or 50 °C, depending upon the anticipated yield, producing 12 or 13 viable analyses at increasing temperatures. The heating duration at each step was 5 min. The precision of the isotopic measurements, as determined by repeated analyses of standard waters and an internal solid standard, are $\pm 0.30\text{‰}$ ($\delta^{18}\text{O}$) and $\pm 0.14\text{‰}$ ($\Delta^{17}\text{O}$) (1σ , standard deviation). Larger error bars on some individual $\delta^{18}\text{O}$ data points reflect the contribution of a small memory effect evident when water samples of greatly differing isotopic composition are measured consecutively during a stepped-heating experiment. Further details of the technique and discussion of the possible sources of error are in Baker *et al.* (2002).

RESULTS

Results from a sample whose size and stepped heating profile were optimised for mass spectrometer analysis are displayed in Table 1 and Fig. 1. The total yield of water from this sample of Tagish Lake was $8.94 \mu\text{mol}$ equating to 3.9 wt% H_2O . This total comprised 13 individual analyses (see Table 1) allowing discrimination between water held in different reservoirs within the sample. The yield is approximately half that of CM samples and only a third of that evolved from CI samples. Sources of water produced during pyrolysis would include that adsorbed to mineral surfaces, that held as interlayer water in smectite-type minerals, together with that originating from O–H groups held within the structure of hydrated minerals. Figure 1 is a plot of the yield and isotopic composition of water liberated at temperature steps between 50 and 800 °C. The lower right-hand vertical axis displays the $\delta^{18}\text{O}$ values of each individual step while the top vertical axis displays the corresponding $\Delta^{17}\text{O}$ values. The release of water from Tagish Lake shows some similarities to both Orgueil and Murchison, representing CI and CM meteorites (Fig. 2). The evolved water defines two clear releases, the first occurring at ~ 150 °C and a second, much larger peak, centred at ~ 550 °C. $\delta^{18}\text{O}$ values show a large range approaching 25‰ beginning at about -4‰ ,

TABLE 1. Water and isotopic data from a stepped-heating experiment with a 4.05 mg sample of the Tagish Lake carbonaceous chondrite.

Temp. step (°C)	Yield H_2O (ppm/°C)	$\delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
50	1.1	–	–	–
100	53.5	–1.9	–4.3	0.0
150	57.9	–0.6	–1.9	+0.1
200	44.4	–0.6	–1.8	+0.1
250	27.3	+0.7	+1.1	–0.2
300	18.8	+2.2	+3.1	+0.3
400	25.8	+3.4	+5.6	+0.2
450	57.2	+7.1	+13.4	+0.6
500	93.3	+11.6	+20.0	+1.0
550	137.3	+13.1	+22.5	+1.2
600	92.1	+12.2	+20.9	+1.0
650	62.3	+10.8	+18.2	+1.0
700	57.0	+11.6	+20.6	+0.7
750	44.3	+11.3	+19.6	+0.8
800	2.2	–	–	–

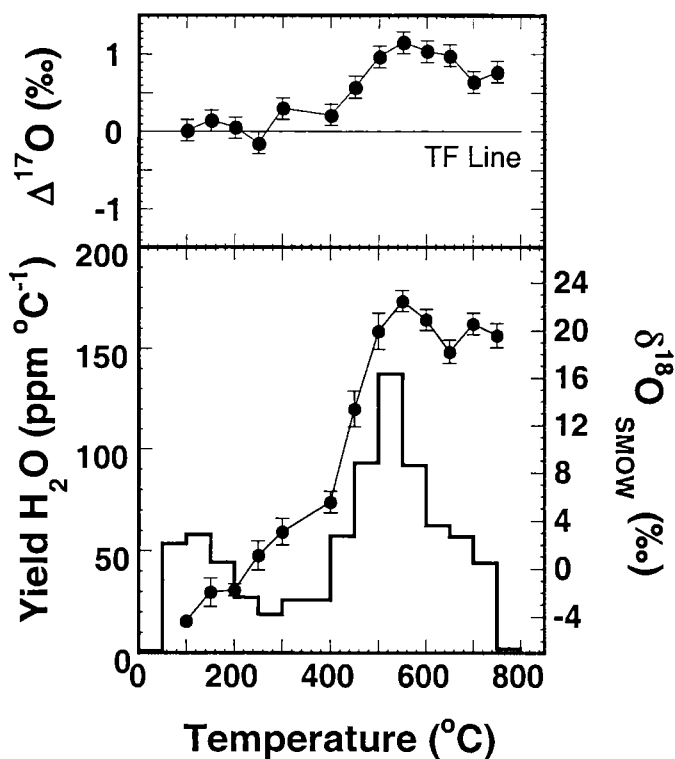


FIG. 1. Water yield and isotopic data from a stepped-heating experiment with a Tagish Lake sample. Yield is represented by the solid line in the bottom half of the plot with values on the left-hand vertical axis. $\delta^{18}\text{O}$ also on the bottom half of the plot correspond to the right-hand vertical axis. $\Delta^{17}\text{O}$ values are shown on the top half of the plot. Errors shown are 1σ in all cases and are derived from measurements of solid standards.

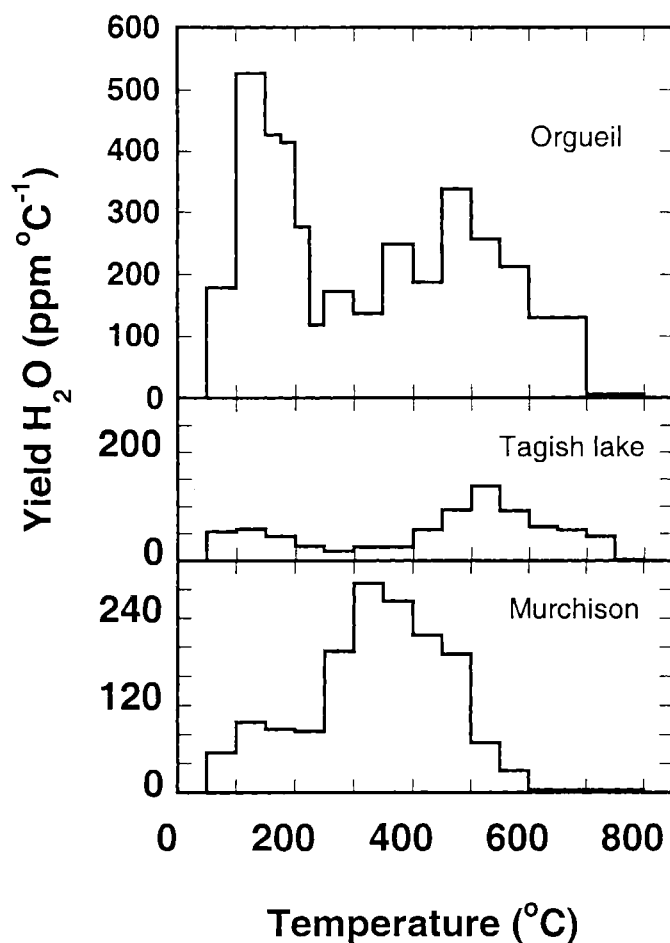


FIG. 2. Comparison of water yields from Orgueil, Murchison and Tagish Lake meteorites during stepped pyrolysis from 0 to 850 °C. Water evolves from Orgueil and Tagish Lake at similar temperatures but with greatly differing absolute quantities.

relative to SMOW (standard mean ocean water), before climbing to a plateau at about +21‰ attained during the second peak in yield. Despite the large range, the majority of water was enriched in both ^{17}O and ^{18}O isotopes and the bulk composition of +13.5‰ ($\delta^{18}\text{O}$) is ~10‰ heavier than for Murchison and 18‰ heavier than for Orgueil.

Perhaps the most important parameter from the point of view of understanding the sources and interactions of water from the sample are the $\Delta^{17}\text{O}$ values. Early steps up to and including that completed at 250 °C display values that lie close to the terrestrial fractionation line (labelled on Fig. 1), which by definition has a $\Delta^{17}\text{O}$ value of 0‰. Water evolved between 300 and ~450 °C displays a gradually increasing trend which culminates in a loosely defined plateau of about +1‰ at steps above 450 °C. Figure 3 illustrates the $\Delta^{17}\text{O}$ values from Tagish Lake compared to Orgueil and Murchison. All three display $\Delta^{17}\text{O}$ values for low-temperature water close to the terrestrial fractionation line but all then deviate at temperatures ~300 °C, after which, water that is clearly not of terrestrial origin predominates.

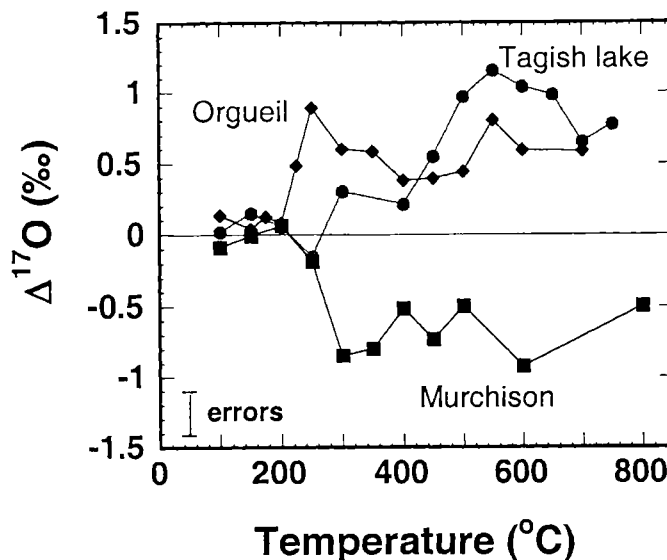


FIG. 3. Comparison of $\Delta^{17}\text{O}$ values from a sample of Orgueil representing typical CI values, Murchison representing typical CM values and Tagish Lake. The terrestrial fractionation line is shown for reference. Errors, as shown, are $\pm 0.14\%$ applicable to all measurements.

DISCUSSION

Bulk Parameters

The analysis of water provides a further very useful tool in highlighting fundamental differences between meteorites of different groups. The results of this study show that the water yield and isotopic data from Tagish Lake differ in detail from both Orgueil and Murchison and, therefore, the CI and CM groups of which these two meteorites are typical. However, some similarities do exist. Figure 2 shows that water yields from Tagish Lake in common with those from analyses of Orgueil and Murchison samples release water defining two peaks, one at low temperature and a second at higher temperature. In the case of Tagish Lake the second water release occurs at a similar temperature to that observed in Orgueil samples, some 200 °C higher than that from Murchison samples.

It is to be expected that an amount of adsorbed water will be released from all samples over the first few temperature steps and that this water will be of terrestrial origin. However, a component displaying terrestrial $\Delta^{17}\text{O}$ values close to 0‰ is apparent to temperatures as high as 400 °C (Figs. 1 and 2) and the quantities of this low-temperature terrestrial component are too large to be purely adsorbed water; this is particularly true in the case of CI chondrites. Tagish Lake is dominated mineralogically by saponite (Mikouchi *et al.*, 2001), a clay mineral of the smectite group that can absorb variable amounts of water between its silicate layers (Grim, 1968). It seems likely that the dominance of saponite together with the high porosity found in Tagish Lake (Gounelle *et al.*, 2001) has

allowed significant quantities of terrestrial water to enter the meteorite and either be absorbed between silicate layers or to isotopically exchange with indigenous water already present—a process that is known to occur readily for such inter-layer water (Savin and Epstein, 1970; Wenner and Taylor, 1974). Although Tagish Lake is dominated by saponites, low-temperature yields suggest that Orgueil has significantly (up to 10×) more inter-layer water than Tagish Lake with a much larger inter-layer to structural water ratio. The Tagish Lake sample studied here has only been above freezing for a few tens of minutes. In contrast Orgueil has been exposed to terrestrial water since 1864 and therefore has had much greater opportunity for absorbing water into the inter-layer sites and for isotopic exchange to occur. If, as seems likely, the increased abundance of inter-layer water in Orgueil compared to Tagish Lake is related to its greater terrestrial age, then this suggests that these meteorites were in fact largely devoid of inter-layer water prior to their arrival on Earth. Such a condition is consistent with the long residence time of the meteorites as small bodies in the hard vacuum of space where any labile water might be expected to be lost by sublimation.

The second main release from Tagish Lake, occurring at a similar temperature to that of Orgueil, may equate to the release of structural hydroxyl groups from smectites. Structural hydroxyl groups are much less prone to isotopic exchange than inter-layer water (Wenner and Taylor, 1974) and therefore should retain isotopic compositions more representative of oxygen originating from an extraterrestrial source, including a component originating from the fluids within which the minerals formed. However, the presence of inter-layer water in smectites renders them more susceptible to isotopic exchange than other hydrated minerals with no inter-layer water (Grim, 1968), for example, the serpentines.

In contrast to Tagish Lake and Orgueil, the release of water from Murchison and other CM chondrites is dominated by a broad release at ~350 °C with only a minor quantity released between 50 and 250 °C (inter-layer or adsorbed water). This is consistent with the mineralogy of the CM chondrites which are believed to be relatively poor in smectite-type minerals capable of releasing inter-layer water during pyrolysis. CM chondrites are dominated, instead, by serpentines (Zolensky and McSween, 1988) which generally accommodate no inter-layer water and which release their structural water at lower temperatures than do smectites (Grim, 1968). While the mineralogic compositions of all the meteorites discussed here are reasonably well established, water release profiles from meteorite samples differ from those derived from experiments with terrestrial hydrated minerals (*e.g.*, Nutting, 1943). As expected, terrestrial saponites release inter-layer water over a range of temperatures prior to loss of the structural water, while serpentines, in contrast, release very little until the structural O–H groups are lost. This pattern of release is observed in the meteorite samples; however, in both saponite and serpentine-group minerals, the loss of structural O–H groups occurred at

higher temperatures than was observed in this study. Possible explanations why the release of O–H groups from meteorite samples showed a lack of conformity to terrestrial analogues are (1) effects resulting from the complex mixture of phases present, (2) variations in the level of crystal perfection of the phases present, and (3) variations of the grain size of the minerals. All these factors are known to affect the temperature at which O–H groups are released from their structural sites (Grim, 1968).

As with yield, $\Delta^{17}\text{O}$ values of Tagish Lake water (Fig. 3) show a greater resemblance to Orgueil than to Murchison. All data representing indigenous water (>450 °C) sits on the same side of the terrestrial fractionation line but with more positive $\Delta^{17}\text{O}$ values than Orgueil. Between data points representing pure indigenous water and low-temperature values with terrestrial signatures are a number of measurements suggesting mixing between the two components. This apparent mixing may be the result of inter-layer water, possessing a largely terrestrial signature, mixing with the first water coming from structural O–H groups, possessing an extraterrestrial signature. The mixing trend between the two end members may also contribute to the $\delta^{18}\text{O}$ data (Fig. 1) but the relatively simple trend in Tagish Lake, reminiscent of that seen in samples of Murchison, is very unlike the complex pattern displayed by Orgueil and other CI meteorites (Fig. 4). The complexity of the $\delta^{18}\text{O}$ pattern displayed by Orgueil and other CI meteorites may be the result of their relatively long terrestrial ages, up to nearly 200 years, allowing greater opportunity for the

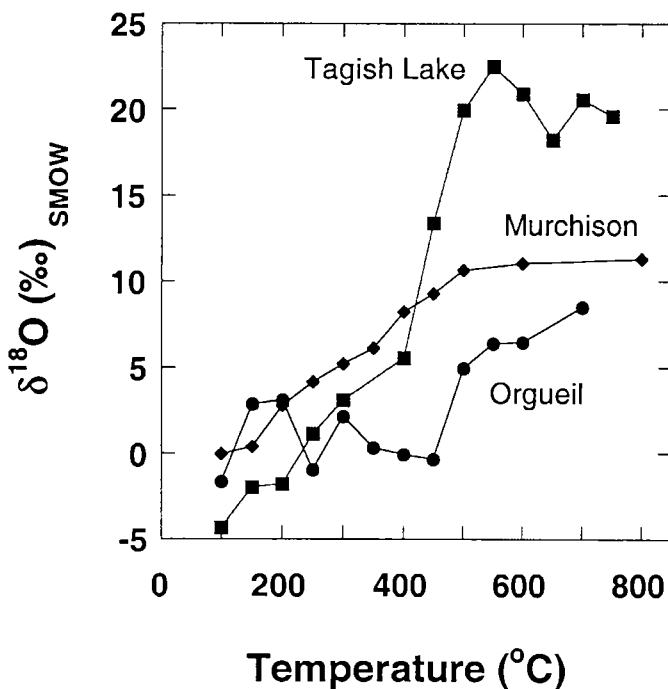


FIG. 4. Plot showing comparison of $\delta^{18}\text{O}$ values from the stepped-heating experiment with Tagish Lake together with values from experiments using Orgueil and Murchison.

development of additional mineralogic reservoirs of water and oxygen. It may be that with greater time the pattern displayed by Tagish Lake may become more complex, a possibility that might be proven if a small amount of Tagish Lake was deliberately left exposed to a moist environment for a period of time. However, the lack of complexity may simply indicate distinct, intrinsic differences between the mineralogy of Tagish Lake and both the CM and CI groups of meteorites.

Comparison of Individual Phases

The relationship, if any, between Tagish Lake and other carbonaceous chondrites can be further investigated by comparison of the isotopic compositions of individual components within each meteorite. In recent years much effort has been given to understanding the processes, both nebular and parent body, that have produced the range of isotopic compositions observed in carbonaceous chondrites and in particular CI and CM meteorites (*e.g.*, Clayton and Mayeda, 1984; Leshin *et al.*, 1997; Young *et al.*, 1999). Models proposed by these workers rely on isotopic measurements of bulk meteorite, refractory anhydrous phases and bulk matrix. Recently, measurements of carbonates (*e.g.*, Benedix *et al.*, 2000) have added to the available data. All these models have assumed that water co-accreting with anhydrous silicates possessed positive $\Delta^{17}\text{O}$ values at or in excess of +2‰, while the anhydrous materials had negative $\Delta^{17}\text{O}$ values (*e.g.*,

Clayton and Mayeda, 1984). Aqueous alteration on the parent body then resulted in evolution of these reservoirs to an extent dependent upon factors such as the water–rock ratio, the temperature of alteration and whether or not reaction took place under open or closed conditions with respect to water. Table 2 shows the bulk isotopic data ($\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ —excluding the low-temperature terrestrial component) from the measurements of water in this study, together with isotopic data from other studies for components of Orgueil (representing CI chondrites), Murchison (representing CM chondrites) and Tagish Lake. The data are illustrated in Fig. 5 where $\Delta^{17}\text{O}$ has been plotted against $\delta^{18}\text{O}$. With $\Delta^{17}\text{O}$ on the vertical axis, the results of mass-dependent fractionation define horizontal lines like the terrestrial fractionation line (shown for reference). It is immediately apparent from this figure that the data for all individual components of Orgueil (in common with Ivuna and Alais which are not shown) are close to defining a single mass fractionation line with a $\Delta^{17}\text{O}$ value near +0.5‰. CI meteorites are commonly believed to have undergone extensive aqueous alteration, obliterating any trace of chondrules or other high-temperature minerals that would once have been present. Such a conclusion is consistent with the relatively well-defined fractionation line in Fig. 5 which suggests that alteration conditions were favourable enough to allow nearly complete homogenisation of the oxygen reservoirs in terms of $\Delta^{17}\text{O}$. This may indicate that alteration continued for a long time or that higher temperatures allowed reactions to occur relatively quickly.

TABLE 2. $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ isotopic values from different components of CI, CM and Tagish Lake carbonaceous chondrites.

	Whole rock		Bulk matrix		Calcite		Dolomite		Water [€]	
	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
Orgueil* [†]	+16.2	+0.39	+17.8	+0.24	+30.3	+0.45	+28.8	+0.41	+3.1	+0.6
Murchison [‡] , [§]	+7.3	-2.60	+12.7	-1.88	+30.5	-0.72	+31.3	-0.78	+11.5	-0.77
Tagish Lake [#] , [§]										
bulk	+18.5	-0.90	+12.2	-0.3 [¥]	–	–	–	–	–	–
carbonate rich [@]					+20.7	+0.8	–	–	–	–
carbonate poor ^{&}	–	–	–	–	+30.9	+0.6	–	–	–	–
					+33.0	+1.4	+35.4	+1.8	+21.0	+1.1

*Orgueil whole rock from Clayton and Mayeda (1999).

[†]Orgueil matrix from Rowe *et al.* (1994).

[‡]Murchison whole rock and matrix from Clayton and Mayeda (1999).

[§]Murchison carbonates from Benedix *et al.* (2000).

[#]Tagish Lake whole rock from Brown *et al.* (2000).

[§]Tagish Lake matrix from Engrand *et al.* (2001).

[@]Tagish Lake "carbonate rich" carbonates (mean value) from Engrand *et al.* (2001).

[&]Tagish Lake "carbonate poor" carbonates and Orgueil carbonates from Leshin *et al.* (2001).

[¥]Value given is the mean of all measurements, which are poorly constrained and have a range in $\Delta^{17}\text{O}$ of ~3‰.

[€]All water data from recent analyses completed as part of this study.

It is not known from which Tagish Lake lithology samples for whole-rock and bulk matrix analysis were taken.

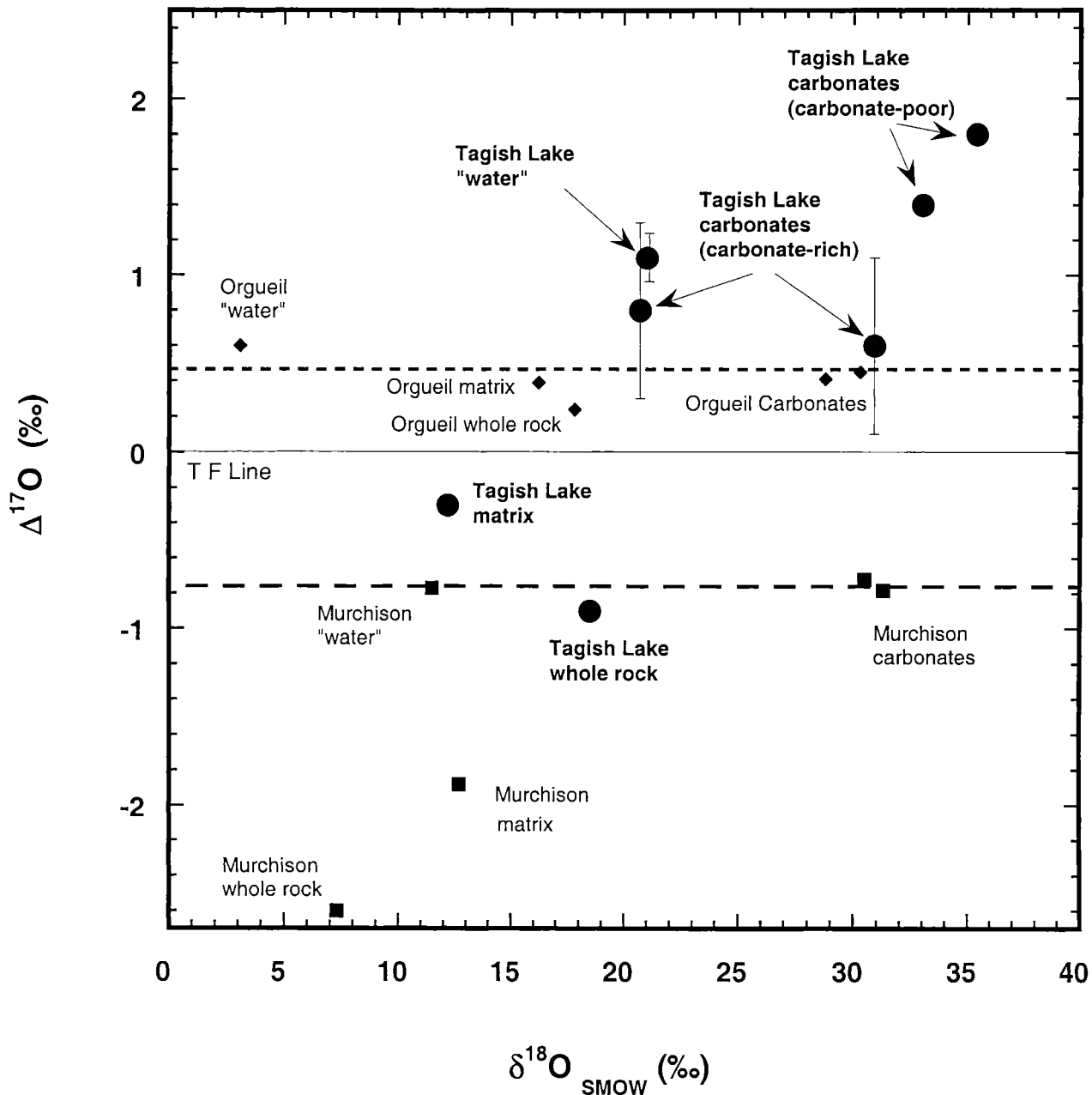


FIG. 5. Plot of isotopic parameters shown in Table 2, with $\Delta^{17}\text{O}$ on the vertical axis. Squares represent Murchison data, diamonds represent Orgueil and circles represent Tagish Lake data. Horizontal lines representing the terrestrial fractionation line and possible mass fractionation on the parent bodies of Orgueil and Murchison are shown for reference. Whereas water and carbonates from both Orgueil and Murchison are close to representing a single fractionation line, the data from Tagish Lake seem to show no such relationship. For data sources, see Table 2.

In CM meteorites, represented by Murchison, the different phases do not show such a well-defined relationship. The oxygen isotopic composition of water, from structural O–H in phyllosilicates, and the carbonates do have the same $\Delta^{17}\text{O}$ values—indicative of a common mass fractionation line—and other CM chondrites analysed such as Murray and Cold Bokkeveld show a similar pattern but at slightly different absolute $\Delta^{17}\text{O}$ values ranging from -0.8 to -1.7% . However, the matrix and whole-rock values lie distinctly below the

fractionation line represented by the water and carbonates. The lack of correlation between matrix values and those measured from water and carbonate may be the result of differences in the isotopic composition of oxygen occupying different structural sites (*i.e.*, isotopic disequilibrium within minerals). It is possible that oxygen forming the basic structural units (the silica tetrahedra), largely maintained their integrity during the alteration process and so retained a greater proportion of ^{16}O originally derived from the anhydrous silicates. This

oxygen would not be released upon pyrolysis for analysis of water, but would be a component of bulk oxygen isotopic measurements from matrix separates where oxygen is released quantitatively. At the same time the structural O–H groups were derived mainly from oxygen and hydrogen within the water. If this is the case then the values we are measuring for the structural O–H groups are in fact close to the actual composition of water taking part in alteration. An alternative possibility is that the matrix samples analysed previously (Clayton and Mayeda, 1984) still contain a component of anhydrous minerals. A number of different approaches were made to produce the matrix separates and each was analysed by x-ray diffraction to ensure that no anhydrous silicates were present. However, x-ray diffraction is not particularly efficient at detecting crystals less than $\sim 0.2 \mu\text{m}$ due to peak broadening (Azaroff and Buerger, 1958). The presence of undetected anhydrous phases in the matrix samples, possessing large negative $\Delta^{17}\text{O}$ signatures, could significantly alter the measured matrix compositions (Franchi *et al.*, 2001).

The identity of the O–H-derived water is crucial to any subsequent calculations of the temperature of alteration. Isotopic fractionation between different components can be compared to experimental results to produce estimates of the alteration temperature (*e.g.*, O'Neil *et al.*, 1969). This is possible because unlike $\Delta^{17}\text{O}$ values, which remain unaffected by mass-dependent chemical processes, $\delta^{18}\text{O}$ values in aqueously altered phases and that measured from the reacting water are subject to mass-dependent fractionation, depending upon the phases concerned and temperature of formation. Estimates based upon the above rely on the assumption that the individual phases were formed at the same time (or at least under the same conditions) or from water with the same isotopic composition.

The similarity of $\Delta^{17}\text{O}$ values for different phases in Orgueil and Murchison, suggesting isotopic equilibrium, allows us to use the $\delta^{18}\text{O}$ data to estimate alteration temperatures. The fractionation between water taking part in aqueous alteration and the resulting phyllosilicates has been calculated for several different phases including serpentines (Wenner and Taylor, 1974; Zheng, 1993). Using the method of Zheng (1993), and assuming intra-mineral isotopic equilibrium (*i.e.*, the O–H oxygen has the same isotopic composition as the other structural oxygen), the fractionation between serpentine and water at 0°C is 26.2‰. When this fractionation is applied to the isotopic composition of water in Murchison it produces a water/carbonate fractionation of 45‰, which in turn would correspond to alteration at a temperature of -33°C , if indeed the level of alteration observed could be accomplished by unfrozen water at that temperature (see Gooding (1984) for suggestions regarding movement and reactions involving films of liquid water at sub-zero temperatures). Alternatively, large $\delta^{18}\text{O}$ fractionations of the above magnitude could be achieved if evolution of the water reservoir by mass-dependent processes, such as partial freezing (which would preferentially remove

the heavier isotopes) occurred, in addition to exchange between ^{17}O -rich liquid and ^{17}O -poor silicates. However, if the value we have measured represented the true isotopic composition of water on the meteorite parent body during alteration (*i.e.*, intra-mineral disequilibrium) then the water/serpentine fractionation could be ignored and the calcite/water fractionation of 19‰ would be equivalent to a temperature of alteration (using O'Neil *et al.*, 1969) of $\sim 80^\circ\text{C}$, a little higher than most models would have favoured (*e.g.*, Clayton and Mayeda, 1984). One possible explanation is that the water composition we are measuring contains a proportion of oxygen in the O–H derived from the anhydrous precursor material (*i.e.*, partial inter-mineral equilibrium) leading to an intermediate water/hydrated mineral fractionation and therefore a larger calcite/water fractionation and a lower temperature of alteration.

In comparison to the oxygen isotopic variation observed in individual CI and CM meteorites, the data (particularly $\Delta^{17}\text{O}$) from different components of Tagish Lake cover a wide range of values indicative of a lack of isotopic equilibrium. It is, therefore, impossible to constrain the temperature at which alteration occurred using calculations based upon fractionation between different phases.

Gounelle *et al.* (2001) noted that two distinct lithologies exist in Tagish Lake, and assuming that they had distinct formation histories this may account for some of the range, particularly that observed for different carbonates. The wide variation of $\Delta^{17}\text{O}$ values in the carbonates may also reflect an evolving water reservoir, with those formed early on possessing a more extreme positive $\Delta^{17}\text{O}$ water composition and those formed later reflecting water having undergone greater alteration by reaction with anhydrous silicates possessing negative $\Delta^{17}\text{O}$ values. A similar record is observed in the CI chondrites but the earlier, more ^{17}O -enriched signatures are restricted to magnetites which are particularly resistant to subsequent isotopic exchange (Rowe *et al.*, 1994). While the isotopic composition of water from Tagish Lake differs slightly from the carbonates, the difference between water and the matrix and whole rock is much greater. The whole-rock $\Delta^{17}\text{O}$ value lies considerably below that of the CI chondrites and the water composition considerably above the CI fractionation line, with a total spread greater than that of the CM chondrites. Assuming similar isotopic compositions for the initial anhydrous silicates and water reservoir to those used in modelling CI and CM chondrites, this is consistent with a lesser degree of hydrothermal alteration in Tagish Lake than CI chondrites as is suggested by the very presence of chondrule remnants, which were used to define Tagish Lake as a type 2 chondrite (Gounelle *et al.*, 2001). In fact the bulk $\Delta^{17}\text{O}$ composition of Tagish Lake would seem to be converging upon a fractionation line somewhere between that of the CI and CM chondrites, giving no indication that the water inventory present during alteration was any larger than that present in CI chondrites. However, all phases do have higher $\Delta^{17}\text{O}$ values than CM chondrites implying a greater isotopic input from

water than that present in CM samples. That reaction and exchange is not as extensive as that observed in CI chondrites may also indicate a lower temperature of alteration.

In attempting to understand Fig. 5, considerable care needs to be taken when comparing data sets, as the large range of isotopic values measured in carbonates might reflect the two different lithologies suggested by Gounelle *et al.* (2001). The sample analysed by Engrand *et al.* (2001) was the carbonate-rich lithology whereas that analysed by Leshin *et al.* (2001) was the carbonate-poor lithology. It is possible that whole-rock and water oxygen isotopic compositions would also vary depending upon the lithology used.

If Tagish Lake originated on a parent body compositionally similar to that of either CI or CM chondrites, then the conditions that prevailed during alteration must have been significantly different from those where the CI and CM chondrites formed. The presence of a wide range of $\Delta^{17}\text{O}$ values in carbonates, none of which appear to be in equilibrium with water, can be interpreted as the marked isotopic evolution of one or two water reservoirs from which phases were formed. The $\Delta^{17}\text{O}$ composition of water could have evolved to its measured value from one compatible with the carbonates measured by Leshin *et al.* (2001). However, if the carbonates in the carbonate-rich lithology were formed from a water reservoir more evolved than that measured in this study (which is uncertain given that error bars from the Engrand *et al.* (2001) data overlap with values measured from water in our study), then either two separate water reservoirs are required or the hydrated minerals we have analysed were formed early and subsequently retained their isotopic composition while the remaining water, from which the carbonate-rich carbonates formed, continued to evolve toward lower $\Delta^{17}\text{O}$ values.

In CI and CM chondrites, similar $\Delta^{17}\text{O}$ values in different phases suggest that the water in which alteration occurred maintained a near constant $\Delta^{17}\text{O}$ value. Water held in a closed or static system should evolve from an initial positive $\Delta^{17}\text{O}$ value to a more negative value during reaction with silicates. It seems likely, therefore, that formation of phases found in CI and CM meteorites occurred under conditions of fluid flow like those of the model of Young *et al.* (1999) where $\Delta^{17}\text{O}$ values could remain stable (although it is noted that evolution of the $\Delta^{17}\text{O}$ composition of water can occur even within the constraints of the fluid-flow model). In contrast, if phases, notably the carbonates in Tagish Lake, accurately reflect a range of $\Delta^{17}\text{O}$ values resulting from evolution of the water in which they formed, this would be more suited to alteration within a closed system where the declining $\Delta^{17}\text{O}$ value of the water reservoir, resulting from continued reaction of water and anhydrous components, was "frozen in" to the carbonates during deposition.

It is unclear whether or not any ordered textural relationship exists between the two lithologies described in Tagish Lake that might help clarify the sequence of hydrothermal events that took place on the parent body. However, if the presence

of two different lithologies was the result of alteration in two unrelated water reservoirs, this would necessarily require some fluid migration—even if the process of alteration and carbonate deposition occurred under static conditions. Therefore, it may be that Tagish Lake formed under conditions incorporating some components of both the fluid flow model of Young *et al.* (1999) and the closed-system model of Clayton and Mayeda (1984, 1999).

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