# Halite and stable chlorine isotopes in the Zag H3-6 breccia

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*Abstract*

Zag is an H3-6 chondrite regolith breccia within which we have studied 14 halite grains ≤3 mm. The purity of the associated NaCl-$H_2O$ brine is implied by freezing characteristics of fluid inclusions in the halite and EPMA analyses together with a lack of other evaporite-like phases in the Zag H3-6 component. This is inconsistent with multistage evolution of the fluid involving scavenging of cations in the Zag region of the parent body. We suggest that the halite grains are clastic and did not crystallise in situ. Halite and water-soluble extracts from Zag have light Cl isotopic compositions, $\delta^{37}Cl$ = -1.4 to –2.8 ‰. Previously reported bulk carbonaceous chondrite values are approximately $\delta^{37}Cl$ = +3 to +4 ‰. This difference is too great to be the result of fractionation during evaporation and instead we suggest that Cl isotopes in chondrites are fractionated between a light reservoir associated with fluids and a heavier reservoir associated with higher temperature phases such as phosphates and silicates. Extraterrestrial carbon released at 600$^{o}$C from the H3-4 matrix has $\delta^{13}C$ = -20 ‰, consistent with poorly graphitised material being introduced into the matrix rather than indigenous carbonate derived from a brine. We have also examined 28 other H-chondrite falls in order to ascertain how widespread halite or evaporite-like mineral assemblages are in ordinary chondrites. We did not find any more to add to Zag (H3-6) and Monahans (H5), which suggests that such highly soluble phases were not usually preserved on the parent bodies.

### *Introduction*

In recent years petrological studies of chondrites have uncovered a record of fluid activity on the earliest planetesimals. Characterising the different types of fluid activity is necessary in order, for instance, to understand the processes behind stable isotope variations (Bridges et al. 1999) and the compositional processing of early Solar System solids (Grossman et al. 2000). In this paper we report the results of a geochemical and mineralogical study into the halite-bearing, Zag H-chondrite regolith breccia and a search for similar minerals in other H-chondrite falls in order to assess how widespread this style of secondary mineralisation is. The geochemical work includes results of a stable chlorine isotope study, mainly of the Zag halite. This offers the potential to help characterise brine fluids together with their mineralogical and isotopic associations within the early Solar System. Volatile elements such as oxygen are incompletely homogenised in planetary bodies, including the chondrites' parent bodies, and so their isotopic compositions have preserved relict reservoirs from the early Solar System. Similarly, Cl-isotopes in chondrites could have preserved distinct reservoir compositions, or they may reflect parent body fractionation processes, and that is one of the issues we address in this paper. Chlorine isotopes have been used in studies of terrestrial rocks to characterise fluid sources and it has been demonstrated that the Earth's mantle $\approx$ +4 ‰ and the exogenic reservoir (dominated by seawater) has $\delta^{37}Cl \sim 0$ ‰ (Magenheim et al. 1995). The total observed terrestrial variation in $\delta^{37}Cl$ is approximately +7 ‰ to - 8 ‰ (Schauble et al. 2003).

Mineralogical evidence for extensive aqueous alteration that might be associated with isotopic fractionation has been found in both the unequilibrated ordinary chondrites (UOCs) and carbonaceous chondrites. In a study of a broad range of ordinary chondrites Grossman et al. (2000) showed that corrosion and bleaching of UOC chondrules was a widespread phenomenon. This style of alteration involved substantial redistribution of the major cations, the corrosion leading to losses of alkalis and aluminium, within the outer margins of the altered chondrules. In another sign of this volatile element redistribution, alkalis and halogens have sometimes been precipitated in UOC matrix as shown by the 'White Matrix' first described by Kurat (1969). The importance of fluid processes in the parent body history of carbonaceous chondrites is also well established as shown by the common presence of phyllosilicates and carbonates in the matrices of these meteorites (Zolensky and McSween, 1988). The presence of widespread aqueous activity in the chondrite parent bodies is associated with both partial

oxygen isotopic exchange between separate isotopic reservoirs and mass fractionation (e.g. Bridges et al. 1999, Clayton and Mayeda, 1984).

The main meteorite used in this study - Zag - is a fall from Morocco 27$^{o}$20'N, 9$^{o}$20'W (August 4th/5th, 1998) totalling at least 175 kg. An initial classification as an H3-6 regolith breccia was given in the Meteoritical Bulletin (Grossman, 1999). A previous description of halite in Zag and the H-chondrite breccia Monahans was also made by Rubin et al. (2002). They described Zag as a matrix-supported breccia comprised mainly of light H5 and H6 clasts, darker clasts that had formed from the light clasts during shock events, and suggested that the halite was derived from in-situ crystallisation from a brine. A CI carbonaceous clast was recently separated from Zag (Zolensky et al. 2003) and that is the subject of a separate study (Zolensky et al. in prep.). Zolensky et al. (1999) also described similar halite grains of up to 3 mm diameter in the Monahans (H5) regolith breccia and reported Rb-Sr (model age of 4.7 ± 0.2 Ga) and microscope heating stage data for aqueous fluid inclusions identified within that halite. The Monahans data were considered to be consistent with a low temperature origin (<100$^{o}$C) of the halite through indigenous fluid activity in the parent body. Barber (1981) noted halite and sylvite grains within a waxy organic mass of 1 mm diameter separated from Murchison (CM2) which is one of the chondrites from which we have prepared a water-soluble extract.

We have also measured the abundance and distribution of carbon in Zag components, in an effort to see whether either the brecciation or any fluid alteration events can be related to the carbon systematics. A slightly enhanced total carbon abundance has been measured in dark clasts relative to light clasts in solar wind gas-rich breccias (Begemann and Heinziger, 1969), although those measurements took no account of possible terrestrial contaminants. The source of the additional carbon was not clear, but it has been assumed that it is related in some way to the shock events that led to brecciation.

### *Samples and techniques*

Most of the Zag petrography was carried out on material separated from a 15 x 10 cm slice (NHM sample 1999, M34). Polished sections of the different clast types and matrix were prepared with non-polar fluids. Several doubly-polished demountable sections were made and these were used for the fluid inclusion work. Some halite grains were directly separated from the cut slice and either retained for I-Xe analyses (Whitby et al. 2000), the Cl-isotope work presented here or our heating stage fluid inclusion study. The thin sections were studied by optical microscope and back-scattered electrons with the SEM.

In addition new polished sections, prepared with non-polar fluids, were made of 28 other H-chondrite falls: Adare (H5), Barbotan (H5), Benld (H6), Bremervörde (H3 breccia), Cangas de Onis (H5 breccia), Ceresto (H5 breccia), Cronstad (H5), Ekh Khera (H6), Forest City (H5 breccia), Gao – Upper Volta (H5 breccia), Gütersloh (H4 breccia), Jamkheir (H6 breccia), Jilin (H5), Kabo (H4 breccia), Kadonah (H6), Khetri (H6 breccia), Lançon (H6), Leighton (H5 breccia), Lixna (H4), Olmedilla de Alarcón (H5 breccia), Pulsora (H5 breccia), Pultusk (H5 breccia), Queen's Mercy (H6), Sharps (H3), Supuhee (H6 breccia), Tieschitz (H3), Wessely (H5), Weston (H4 breccia). These were analysed using optical microscopy and back-scattered electrons.

Mineral analyses of Zag sections were made using a Cameca SX50 electron microprobe at 15 kV, 20 nA. The fluid inclusion work was made on demounted sections of Zag or separated pieces of halite using a Link heating/cooling stage MDS600. This is the first reported heating stage work for the Zag halite although Rubin et al. (2002) made observations on the morphology of fluid inclusions of this material.

Water-soluble extracts for the chlorine isotope and halogen analyses were prepared from halite and powdered H4 matrix from Zag. The samples were put in sealed tubes with deionised water, agitated, and heated in a boiling water bath for several days. Analyses of $^{37}Cl/^{35}Cl$ were carried out with thermal ionisation mass spectrometry by the technique of Banks et al. (2000). To further characterise brine compositions halogen (Cl⁻, Br⁻, F⁻), sulphate and some other major element concentrations were determined by ion chromatography on the same extracts. Extracts were also analysed from powders of the CM2 fall Murchison and the H5 find Plains providing a comparison with terrestrially contaminated

chondritic material.  Other meteorites (Weston H4, Tysnes H4, Cold Bokkeveld CM2) released too much dissolved matter for successful mass spectrometry.

$\delta^{37}Cl$ is relative to Standard Mean Ocean Chloride (Long et al., 1993):

$$\delta^{37}Cl = \left(\frac{R}{R_o} - 1\right) \times 1000$$ where R and $R_o$ are the measured $^{37}Cl/^{35}Cl$ ratios of the sample and standard.

The abundance and distribution of carbon in three samples from Zag (an H5 clast, a light-coloured H6 clast and the clastic, H3-4 matrix) were determined by high resolution stepped combustion mass spectrometry at the Open University, using the modified MS86 gas extraction and mass spectrometer system. A small chip (5-10 mg) of each sample was wrapped in platinum foil and heated in the presence of oxygen in increments between room temperature and 1400°C. After cryogenic separation from the by-products of combustion ($H_2O$, $SO_2$), the $CO_2$ yield was measured on a capacitance manometer. Aliquots of $CO_2$ were then admitted to a triple collector noble gas-type mass spectrometer for isotopic analysis. As for the chlorine data, carbon isotopic compositions are reported in the  notation, relative to the PDB international reference. A typical total blank for the system (RT-1400°C) was around 7 ng carbon with a $^{13}C \sim$ -25 ‰; errors on yield were ± 0.2 ng, and on the isotopic composition ± 0.5 ‰.

### *Zag petrography*

The main meteorite slice shows a brecciated texture with 3 discrete components: 65% light-coloured clasts and 25% surrounding grey H3-4 (i.e. not entirely equilibrated during thermal metamorphism) clastic matrix with some well-defined chondrules. Lesser amounts (~10%) of a dark clast-type (H5) are also present. The light clasts studied here are H6(S3), Rubin et al. (2002) also identified H5(S2) and H6(S4) light clasts in their sample of Zag indicating that there is some heterogeneity in the clasts between samples. The matrix is shock stage S3 and similarly none of the mineral grains in our 1 cm sectioned part of a dark H5 clast have the diagnostic signs (Stöffler et al. 1991) to be numbered with a higher shock stage. However, some of these dark clasts in other samples of Zag are S4 (Rubin et al. 2002) and all the dark clasts show numerous scattered microscopic veinlets of iron and sulphide blebs which are characteristic of limited shock effects. We did not identify any bleached or corroded chondrule margins within Zag beside halite or elsewhere in our sections.

The light clasts have an equilibrated olivine composition of Fo80.6 (80.4–81.4, n=13) and low-Ca pyroxene En81..8Fs16.6 Wo1.6 (range 80.5-82.7, 15.8-17.7, 1.4-1.9, n=13). The dark clasts have similar compositions: Fo81.6 (79.1-81.5, n=19); En 82.3 Fs 16.3 Wo 1.4 (81.3-82.6, 15.8-17.4, 1.2-2.2, n=8). Minor high-Ca pyroxene e.g. En71.6 Fs13.8 Wo14.6 is also present in the matrix and clasts. The matrix is heterogeneous in terms of its degree of variation in mineral compositions between various sections, with the analyses in one section showing apparent equilibration. However, the average compositions for matrix olivine and pyroxene grains analysed here within 3 sections are: average Fo 81.6 (77.9-96.0, 1 sd = 2.4, n=42); En83.5 (80.5-96.5, 1sd=3.8, n=27), Fs15.0 (3.3-17.7, 1sd =3.5), Wo10.52 (0.27-9.7, 1sd=1.7). As the average En and Fo molar contents of the low-Ca pyroxene and olivine are both slightly higher in the matrix than for the minerals in the clasts this indicates that the H3-4 matrix has a more Mg-rich bulk composition than the clasts.

Ten halite grains (≤3 mm diameter) have been identified on the cut surfaces of our Zag sample and 4 others have been found in our thin sections, all 14 are within H4 parts of the matrix (e.g. Fig. 1a). The grains are not present along obvious veins, although some of their outlines (i.e. rhombohedral in the case of the largest one) indicate that they have undergone simple shear: that is deformation with constant volume from an initially euhedral, cubic grain outline. Some of the halite grains also show signs of having undergone recrystallisation during deformation. This is shown by the development of

subgrains e.g. Fig. 1b. The halite grains in thin section and hand specimen have mottled colours varying from near colourless to blue (predominant) and dark blue.

No other minerals within Zag which might have a related paragenesis to the halite e.g. carbonates, sulphates or clay veins have been found, the textures and silicate mineral assemblages seen in thin section are typical of H-group breccias. The only indication of other salt minerals was obtained from the analysis of water-soluble extracts, which might show that $MgCl_2$ is present (see below). Some slight corrosion has occurred on one surface of the Zag specimen as shown by the presence of orange ferric oxides. This is assumed to be terrestrial in origin and does not appear to have affected the silicate or halite.

The halite is nearly pure NaCl as K $\leq$0.04, S $\leq$0.04, Br $\leq$0.15 wt%. These upper limits were determined by multiple analyses within 2 separated grains and 3 grains in thin section. No sylvite (KCl) grains were identified.

### *Fluid inclusions in halite*

Halite contains fluid inclusions (≤30 μm), occupying up to 5 vol. % of one grain, and these were studied on a heating stage using separated grains and a doubly polished, demounted thin section. The halite was found to contain both primary and secondary fluid inclusions. Those assumed to be primary are present along cleavages and those with a secondary origin are present along cross-cutting fractures (Fig. 2). Problems may occur in identifying truly primary inclusions in halite, due partly to the possibility of trapping secondary inclusions along growth face-parallel cleavage planes, and to the ease with which the mineral may re-crystallise (Roedder, 1984). However, the presence of two texturally definable populations (large, cleavage parallel and isolated inclusions, and cross-cutting planar trails) suggests that at least one group can definitively be said to be earlier than the other, and in the case of the large isolated inclusions these are likely to be primary.

Liquid plus vapour to liquid homogenisation temperature ($T_h$) measurements are difficult to make in halite as a result of modification of inclusions both in nature, and during the course of measurement (Roedder, 1984). In this case we found that attempts to repeat measurements of $T_h$ resulted in an increase in $T_h$ with each successive measurement. A typical set of $T_h$ runs on the heating/cooling stage provided an initial $T_h$ of 20$^o$C, followed by a second one of 40$^o$C and a third of 50$^o$C. This implies stretching of the halite, possibly along cleavage planes, as a result of increased internal pressure on heating. In all cases, therefore, the first values of $T_h$ obtained on the inclusions (~ 20$^o$C – 40$^o$C) are interpreted as a more reliable indication of fluid density. The low $T_h$ values and the lack of vapour bubbles at room temperature is consistent with formation <70$^o$C, although an independent pressure estimate is not available to correct $T_h$ to a trapping temperature.

Following cooling to –100$^o$C the majority of inclusions showed the initial formation of liquid at ~-28$^o$C, consistent with the metastable eutectic ($T_e$) of ice plus NaCl plus liquid in the system NaCl-$H_2O$ (Roedder, 1984). When held at -27.8$^o$C for 15 min., fluid inclusions contained a mixture of hydrohalite $NaCl.2H_2O$ (including that formed through corrosion of the inclusion margins), ice and vapour. These data suggest a predominantly NaCl-$H_2O$ brine. They do not prove the absence of K, the presence of which would not greatly affect the $T_e$ but they are compatible with the near pure halite composition determined by electron microprobe. In contrast, Monahans inclusions (Zolensky et al., 1999) showed eutectic melting at ~ -40$^o$C indicating the presence of other cations in the fluid and consistent with the presence of sylvite inclusions within that halite.

### *Other H-chondrite breccias*

No halite, salt or clay minerals were identified in any of the other 28 H-group breccia fall samples studied (listed above). This is an indication of the rarity of these phases in H-chondrite breccias. Halite mineralisation is clearly a less common form of low temperature fluid activity than the corrosion and bleaching shown to be commonplace in UOC chondrules by Grossman et al. (2000). This corrosion was also found by those authors in some equilibrated OCs. If the hydrous fluids associated with bleaching acted to dissolve soluble minerals, that may be the reason halite has only been preserved in a small proportion of chondrites.

An alternative explanation is loss of halite during the meteorites' residences on Earth. This is possible, as shown for instance by the apparent absence of halite in some other stones of Zag we have studied which may not have been recovered quickly after the fall. However, we feel it is likely that macroscopic halite would have been spotted in other H-chondrite falls, either in our study or by others if halite was typically associated with this meteorite type.

### Bulk chondrite halogen abundances and effects of terrestrial contamination

The Na and $Cl^-$ contents in the Zag matrix extract (Table 1) suggest that the extracted Cl was mainly derived from halite. However, the excess of $Cl^-$ relative to Na implies that there may also be other, unidentified phases which have not been identified in thin section or that some of the chlorapatite in Zag was dissolved during the water extraction.

The low contents of $SO_4$ in the Zag matrix extract are consistent with the absence of sulphate minerals in the thin sections studied. In contrast, the very high $SO_4$ contents within the extracts of Murchison and Plains are of more ambiguous origin. The latter find could have gained terrestrial sulphate. For instance, the CI chondrite Orgueil contains 4.7 wt% $SO_4$, in water-soluble extract (Fredriksson and Kerridge, 1988) but it is not certain what proportion of this is extraterrestrial in origin (Gounelle and Zolensky, 2001). However, even if the sulphate contents of Plains and Murchison are partly or mainly derived from terrestrial contamination it does not appear to be associated with the addition of appreciable amounts of Cl contamination because the $Cl^-$ contents of Zag matrix, Plains and Murchison are all similar and relatively low. The Na and $Cl^-$ contents of our Murchison extract are consistent with the presence of halide (Barber, 1981). The soluble Cl-phase in Plains has not been identified, although from the low Na content of our extract, it is unlikely to be halite.

Dreibus et al. (1979) used a pyrohydrolysis technique to determine that the mean bulk Cl content of CI chondrites was 688 ppm, and two CM2 chondrite falls (Murray and Murchison) had an average Cl content of 183 ppm. Dreibus et al. also calculated Br contents in bulk Murchison (0.61 ppm; Br/Cl = 0.003). Anders and Grevesse (1989) gave an average compilation Br/Cl wt. ratio for CI chondrites of 0.0051.

The bulk Cl abundances of a range of chondrites were determined by Garrison et al. (2000) using the irradiation $^{37}Cl$ (n,$\gamma$) $^{38}Ar$ and a stepwise degassing technique. In this way they were able to distinguish between low- and high-temperature components. The range of bulk OC chlorine abundances was 15-177 ppm, mean = 91 ppm, and the proportion of Cl released at low temperatures varied from 0-61%, mean = 13.7%. As the low temperature Cl component was most abundant within stony meteorite finds rather than falls, Garrison et al. suggested that any terrestrial contamination formed part of this proportion of the total Cl content. Goles et al. (1967) published a Br/Cl ratio range of 0.0001 to 0.022 for ordinary chondrite falls.

Langenauer and Krähenbühl (1993) and Krähenbühl and Langenauer (1994) determined that most halogen contamination in stony meteorite finds was located near the surface of the meteorites e.g. a few mm thick zone. Meteorite identified away from the coast towards the Antarctic interior have experienced less F, Cl, Br contamination. They further demonstrated that the halogen contamination of Antarctic H5 and H6 finds correlated with their terrestrial age. Therefore samples taken from the interior of meteorites will not show significant contamination of Cl-isotope compositions.

In summary, these studies of $SO_4$ and Cl abundances in other meteorites suggest that the effects of Cl contamination in our analyses will not be great and that it is likely original Cl-isotopic ratios of the water-soluble extracts from the Zag matrix and Plains have been preserved. The higher Br/Cl ratios of extracts from Plains might suggest that terrestrial adsorption of halogens can act to increase Br/Cl ratios. This might also be expected to alter the $\delta^{37}Cl$ values but the data available suggest that adsorption of aerosols tends to increase $\delta^{37}Cl$ (Magenheim et al. 1994), so again there is no obvious sign of Cl contamination. Therefore the study of Cl-isotopes in chondrites need not be prohibited by the issue of terrestrial contamination although care would be necessary to avoid samples sampled near coastlines or of great terrestrial age e.g. Langenauer and Krähenbühl (1993). The Zag halite was sampled pure so terrestrial contamination can be ruled out for it.

### *Br/Cl brine ratios and Cl-isotopic values*

The Br/Cl ratio (0.0014) of the Zag halite lies within the large range of OC falls (0.0001 – 0.022, Table 1 and above). Similarly, halite from the Monahans meteorite has a Br/Cl ratio of 0.003 - 0.009 determined by EPMA (Rubin et al. 2002). However, the Br/Cl ratio determined on bulk Zag matrix (using a similar technique to that employed by Garrison et al. 2000; Whitby et al. 2000) is 0.017, suggesting that other, non-soluble phases e.g silicates and phosphates contributed to that bulk Br/Cl ratio. The identification of halite in Murchison (Barber, 1981) may also indicate that the Br/Cl ratio (0.0023) in the water-soluble fraction of that CM chondrite is dominated by that phase.

Zag halite and the silicate extract have light chlorine isotopic values compared to bulk carbonaceous chondrites (Magenheim et al. 1994, 1995) (Fig. 3). There is a difference of 5 to 7 per mil between the water-soluble extracts, including halite, and the bulk chondritic pyrolysis values from (Dreibus et al. 1979; Magenheim et al. 1994, 1995). This might indicate that the halite values are fractionated from a primordial early Solar System reservoir or it might mean that there were at least two separate reservoirs in the early Solar System – a heavy one at $\delta^{37}Cl \approx +3$ - $+4$ ‰ (represented by the bulk chondritic values) and a light one at one at $\delta^{37}Cl \approx -1.5$ to $-3$ ‰ (represented by our analyses).

## Carbon abundances and isotopic compositions

In an extensive study of carbon in ordinary chondrites, Grady et al. (1989) found that all the samples they studied (finds, falls, Antarctic, non-Antarctic) contained varying amounts of terrestrial contaminants, from a combination of weathering and other sources. The contaminants combusted at temperatures below around 400 - 500°C. The results from Zag given in Table 2 also show that, even though the meteorite is a recent fall, it has also suffered from the ubiquitous organic contamination. In our discussion of the carbon results for Zag, therefore, we regard carbon that combusts below 400°C as being contaminant. Results from the carbon analysis of matrix from Zag are plotted in Figure 4a. There are two maxima in the carbon release, at T ~ 600°C and T ~ 850°C. The higher temperature is characteristic for combustion of crystalline graphite, and the $\delta^{13}C$ of -21 ‰ is fairly typical for graphite in ordinary chondrites (Grady et al., 1989). The lower temperature maximum could be either from decomposition of a calcium-rich carbonate, or combustion of less well-crystalline graphite. We suggest the $\delta^{13}C$ of -20 ‰ is more typical of the reduced carbonaceous component rather than a carbonate (Grady and Wright, 2003); given that (a) the abundance of this component is approximately equal to that of the graphite, (b) its $\delta^{13}C$ is very similar to the graphite and (c) no trace of carbonate was found in the matrix, then it is likely that the lower temperature component is a poorly-crystalline graphite.

The two clasts have very similar carbon abundances and yield-histograms (Figure 4b, c). There is no single discrete maximum – the dominant feature in both samples is the combustion of remnant contaminant species up to 550°C. The variation in carbon isotopic composition is also similar across the two clasts, with a minimum in $\delta^{13}C$ of –35 to -30 ‰ at 1000°C.

*Discussion*

The presence of halite within a metamorphosed chondrite is anomalous. Thermal metamorphism of halite-bearing assemblages is associated with the crystallisation of scapolite (Orville, 1975) which is not present in Zag. As there are no reaction rims between the halite and surrounding silicate the Zag halite grains did not experience the thermal metamorphism that the silicate phases underwent in the H3-4 matrix (e.g. ~600°C). It is also unlikely that the fluid inclusions within the halite could have been preserved at elevated temperatures. There are two potential explanations for the presence of unmetamorphosed halite within the Zag matrix. Firstly the halite grains could have crystallised from a brine in a short-lived evaporation event during the waning stages of, or after, the metamorphism associated with the type 3-4 matrix, prior to final aggregation of the more highly metamorphosed Zag material. Alternatively, the grains were incorporated along with a mixture of already partially metamorphosed H3-4 matrix, H6 clasts and occasional, carbonaceous chondrite material. The absence of halite in the clasts suggests that the crystallisation of halite did not postdate the final aggregation of the different chondritic materials.

In the first model, the halite could be an end product of the evaporation of a brine but the absence of other soluble products, notably carbonates and also clays in the Zag H3-6 materials makes this unlikely. The absence of a solar wind Xe signature e.g. large amounts of $^{132}$Xe (Whitby et al. 2000), also seems to rule out this scenario because it means that the halite has not undergone the same regolith history as the matrix. Similarly, the purity of the brine indicated by the fluid inclusion studies and the absence of any evidence for chondrule corrosion in Zag is difficult to reconcile with an origin through corrosion of the immediate vicinity of the parent body.

The Br/Cl ratio of terrestrial seawater (0.0035) is higher than the range of Br/Cl ratios (0.0001 to 0.0005) expected for halite precipitated from seawater (Sonnenfeld, 1984). Furthermore, the general trend associated with the precipitation of halite and other evaporitic salts, is an increase in residual Br/Cl ratios. By analogy with this, the Zag halite does not appear to have been fractionated by extensive salt precipitation because its Br/Cl ratio lies within the range of OC falls. This suggests that the halite was not an end product of fluids which had undergone fractionation e.g. through cycles of

crystallisation and redissolution in an extensive and long-lived hydrothermal system on the Zag parent body.

Therefore the second scenario of halite grain incorporation at the same time as the various clasts and H3-4 matrix is considered most likely, and in contrast to Rubin et al. (2002) we suggest that the halite is clastic and did not crystallise in-situ. The Zag matrix has small but discernibly higher Mg contents than the H clasts suggesting that the brecciation mixed together compositionally different H-chondrite material.

The carbon data from the two clasts are very similar to that obtained on other H-group chondrites of high petrologic type (Grady et al., 1989). In contrast, carbon in the matrix is much more abundant, by about an order of magnitude, although its isotopic composition is very similar to that of the clasts. This is usual for ordinary chondrites. There are two distinct components of carbon present in the matrix, each of distinct crystallinity. It is likely that the lower temperature material is poorly-graphitised carbon introduced into the matrix during brecciation, in the same way as has been observed for other brecciated ordinary chondrites (Scott et al., 1988).

Previously reported I-Xe data for some halite grains from Zag have been interpreted as ages 5 Ma later than Shallowater with a scatter in ages due to parentless $^{129}$Xe trapped in secondary fluid inclusions (Busfield et al. 2004). The same authors also reported Ar-Ar data for silicate and halite separated from the Zag meteorite in order to constrain the timing of this fluid activity in relation to other early Solar System processes. The Ar-Ar ages for the matrix and an H6 clast were indistinguishable at $4.25 \pm 0.03$ Ga. This may be the age of lithification of the various Zag components. One analysis of a halite grain also gave a later Ar-Ar age of 4.0 Ga. This suggests that some of the brecciation of the halite grains took place after their accretion with the other Zag components. The colours of the halite are due to colouration during ionizing radiation. This is a result of excess electron centres and holes being formed in the lattice structure – and hence the blue/violet colour effects seen in the halite - but this only occurs at low temperatures and is lost at high temperatures (Schulman and Compton, 1962; Nassau, 1978). Combined low temperatures and ionising radiation would be experienced on the surface of the parent body prior to ejection or during the meteoroid's passage from the asteroid belt to Earth.

## *Chlorine isotopes: fractionation or a reservoir composition?*

The fractionation factor $10^3 \ln\alpha$ for the ratio $^{37}Cl/^{35}Cl$ between halite and brine is 1.00026 (Eggenkamp et al. 1995). This low figure implies that Cl-isotopes will have experienced little isotopic fractionation between the parent brine and the halite precipitate now found as grains within the Zag matrix. For instance, Eggenkamp et al. (1995) demonstrated that complete evaporation with related crystallisation of salts fractionates Cl-isotopes by $\leq0.4$ ‰ relative to a parent brine. Even multiple episodes of evaporation and dissolution of salts could not readily explain the difference in $\delta^{37}Cl$ between previously published bulk chondritic values and our water-soluble extracts. This is also consistent with the small range of $\delta^{37}Cl$ values in terrestrial evaporites ($0 \pm 2$‰, Ransom et al. 1995).

$$\alpha = -\frac{(^{37}Cl/^{35}Cl)\,precipitate}{(^{37}Cl/^{35}Cl)o}$$
Fractionation factor $\alpha$ of Cl-isotopes between precipitate (halite) and brine ($o$).

The light Cl-isotope compositions of the Zag halite and water-soluble extracts, compared to the bulk chondrite compositions available, are not therefore the result of short evaporation processes but instead are either the result of fractionation during more extensive, unidentified fluid activity or the relict of an original light Cl-isotope reservoir.   It is known that at equilibrium $^{37}Cl$ is concentrated in substances where $Cl^-$ is bonded to +2 cations e.g. sheet silicates relative to +1 cations e.g. NaCl by 2 – 3 ‰ at 298 K (Schauble et al. 2003).  Organic molecules with C-Cl bonds and oxidised $Cl^+$ and $Cl^o$ can concentrate $^{37}Cl$ to a much greater extent but these are unlikely to feature as significant reservoirs of Cl components within the chondrite parent bodies.

An example of $^{37}Cl$-enrichment is shown by studies of terrestrial Cl-bearing hydrothermal systems which have revealed that smectite clay can have compositions of $\delta^{37}Cl = +7.5$ ‰ (Ransom et al. 1995; Magenheim et al. 1995). This type of clay is also present in chondrites showing signs of aqueous alteration (e.g. Tomeoka and Buseck, 1988) and such a phase might, if present, act to fractionate the Cl-isotopes from $\delta^{37}Cl = +3$ ‰ (bulk chondrites, Dreibus et al. 1979) towards the values we report for the halite. Ransom et al. (1995) also suggested that the crystallisation of clays in hydrothermal systems would act to fractionate Cl isotopes,.  Residual brines such as that envisaged for Zag would have light $\delta^{37}Cl$ compositions. However clay is notably absent from Zag and this together with the purity of the brine means that there is no basis to consider that equilibrium silicate-halite

isotopic fractionation took place on the parent body. Instead we suggest that the Cl-isotopic compositions of Zag and Plains water-soluble extract reported here represent part of a light Cl-isotopic reservoir from the early Solar System. In the next section we briefly note how this model may fit in with what is already known about D/H and oxygen isotopes affected by parent body fluid processes.

## *Stable isotopes in OC fluids*

The large variations in $\delta D$ of $>+4000$ ‰ in chondritic minerals may be the result of fractionation processes associated with parent body fluids, or, the preservation of pre-Solar isotopic anomalies (Robert et al. 2000; McKeegan and Leshin, 2001). The oxygen isotopic compositions of OC materials seem more clear and are determined by mineralogically controlled exchange processes between $^{16}O$-rich solid and $^{16}O$-poor fluid reservoirs. For instance, feldspar and glass separated from the most unequilibrated whole OCs analysed so far has $\delta^{17}O = 6.4$ ‰, $\delta^{18}O = 9.5$ ‰ compared to olivine/pyroxene isotopic compositions of $\delta^{17}O = 3.3$ ‰, $\delta^{18}O = 5.1$ ‰ (Bridges et al. 1999). This relationship, which appears to hold for all OCs, is the result of preferential exchange by framework silicates with ($^{16}O$-poor) fluids. There is probably no direct link between the formation of $^{16}O$-poor and low $^{37}Cl/^{35}Cl$ reservoirs but our work does provide further evidence that fluids associated with chondrite parent bodies in the early Solar System were associated with distinct isotopic reservoirs.

## *Conclusions*

The Zag halite crystallised from the final evaporation products of a brine at <70$^{o}$C. This is shown by the low temperatures of homogenisation of fluid inclusions and lack of vapour bubbles in the halite at room temperature. Fluid inclusion studies also indicate that the brine had a nearly pure NaCl-$H_2O$ composition. The slightly differing Mg content of matrix and clasts indicates that the components of Zag were assembled from different parts of the parent body. We suggest that the halite did not crystallise in-situ but is clastic, incorporated into the Zag H3-4 matrix after that had undergone thermal metamorphism. The halite underwent fracturing and strain-induced recrystallisation around the margins of some grains, both during and, perhaps in some cases, after accretion.

The Br/Cl ratios of the halite and water-soluble extracts of other chondrites are however consistent with derivation of the brines from an ordinary chondrite source. The Cl-isotopes of the Zag halite at $\delta^{37}Cl$ = -1.4 to –2.8 ‰ are about 5 ‰ lighter than previously reported bulk carbonaceous chondrite values. The absence of mineralogical evidence for extensive-fluid rock reactions and purity of the parental brine suggest that the light Cl-isotope compositions are part of a more extensive light Cl-isotope reservoir rather than due to mineralogically controlled fractionations.

The carbon systematics of clasts within Zag are consistent with the presence of graphite and do not appear to have been altered by brecciation and re-aggregation. In contrast, some of the carbon in the matrix is associated with poorly graphitised material which may have been introduced or remobilised during brecciation. It is not likely to be associated with carbonate.

As Zag and Monahans are the only two H-chondrite falls, including 28 others we have examined, within which halite has been identified it is clear that the evaporation of brines near OC parent body surfaces with associated crystallisation and presumed transport of halite during impact processes was relatively uncommon or rarely preserved compared to other types of hydrothermal alteration.

*Acknowledgements*

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Table 1. Cl-isotope, water-soluble halogen and cation compositions.

| | powder wt. (g) | $F^-$ | $Cl^-$ | $Br^-$ | $SO_4^{2-}$ | Na | K | Ca | Mg | Ni | Fe | $\delta^{37}Cl$ | Br/Cl | Cl/Na (at.) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Zag halite-1 | | 0.087 | 5.627 | 0.008 | 0.014 | | | | | | | -1.9 | 0.0014 | |
| Zag halite-2 | 3.188 | 0.035 | 6.597 | 0.009 | nd | | | | | | | -1.4 | 0.0014 | |
| Plains (H5) | 3.188 | | 0.418 | 0.319 | | 0.011 | 0.004 | 0.253 | 0.060 | 0.269 | 0.064 | -2.9 | 0.0028 | 25.4 |
| Zag matrix | 2.127 | | 0.627 | 0.375 | 0.06 | 0.278 | 0.010 | 0.008 | 0.054 | nd | nd | -2.8 | 0.0024 | 1.5 |
| Murchison (CM2) | 2.394 | | 0.627 | 0.344 | | 1.216 | 0.107 | 1.328 | 1.759 | nd | nd | | 0.0023 | 0.3 |
| [1,2] Bulk CI | | 60.7 | 704 | 3.57 | | | | | | | | 2.7 | 0.0051 | |
| [3]Bulk OC falls | | 119 | 91 | ≤1.4 | | | | | | | | | 0.0001-0.022 | |

Element and $SO_4$ analyses in ppm, $\delta^{37}Cl$ relative to SMOC standard. Water-soluble cation and anion contents are quoted for the bulk meteorite (calculated using the powder weight), except for Zag-1 and Zag-2 halite which are compositions of the water-soluble extracts. Bulk (ie water-soluble and insoluble) halogen contents of CI and OC falls listed for comparison. [1]Anders and Grevesse (1989), [2]Cl-isotope ratio for Orgueil from Dreibus et al. (1979). [3]Goles et al. (1967), Garrison et al. (2000), Mason (1971). Fe is total dissolved iron. Cl/Na column is atomic, Br/Cl is weight ratio. nd means species analysed but not detected.

Table 2.  Carbon abundances and isotope data for Zag (NHM 1999, M34)

|  | Weight (mg) | [C] total (ppm) | $\delta^{13}C$ (Total) ‰ | [C] (T>400$^{o}$C) ppm | $\delta^{13}C$ (T>400$^{o}$C) ‰ |
| --- | --- | --- | --- | --- | --- |
| Matrix | 3.666 | 2170 | -22.0 | 1304 | -21.4 |
| H5 clast | 6.614 | 156 | -19.5 | 97 | -21.7 |
| H6 clast | 10.626 | 753 | -24.3 | 101 | -21.3 |

**Figures**
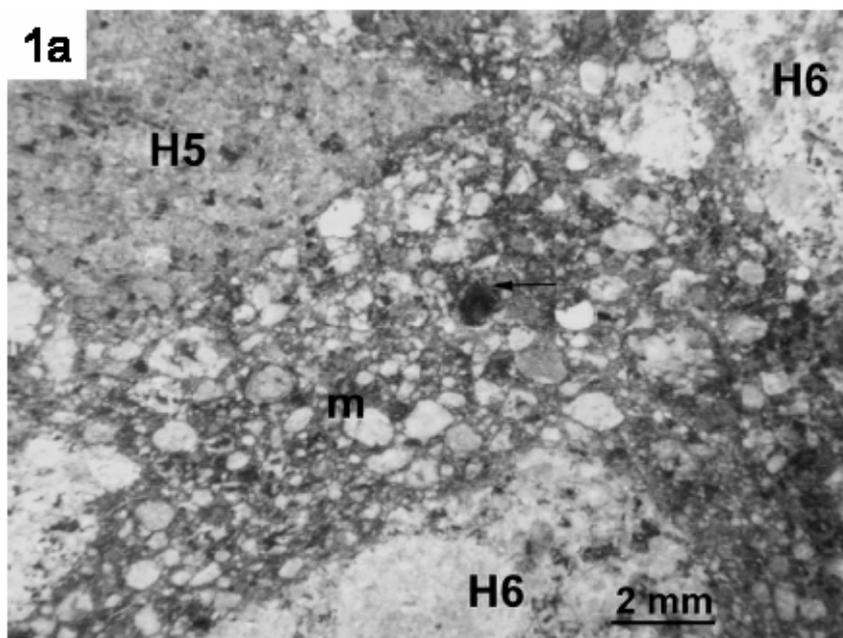


Fig.1a. Halite grain on the surface of Zag breccia. The arrow points to top margin of the halite grain showing that it has been partly fractured. H3-4 matrix (m) with visible chondrules and H5 and H6 clasts are seen. The Zag halite grains do not show evidence in the form of being part of veins or association with other low temperature mineral assemblages for crystallisation in-situ but instead appear to be clastic.
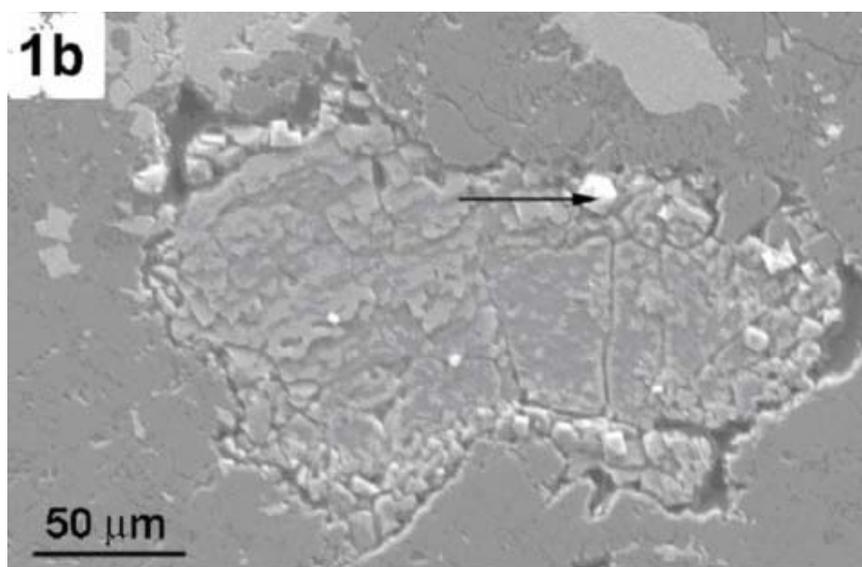


Fig.1b. Halite in Zag. There is some recrystallisation of the halite (e.g. arrowed), some of which - as around the lower margin - may be strain-induced. Secondary electron image, 20 kv.

Fig.2. Fluid inclusions in halite grain from Zag. Arrows point towards ice and hydrohalite (the latter formed through corrosion of the fluid inclusion margins) when held at $-27.8^{\circ}$C. h halite. A trail of secondary fluid inclusions following a fracture can be seen on the left hand side of the image. Image taken on Linkam heating stage.
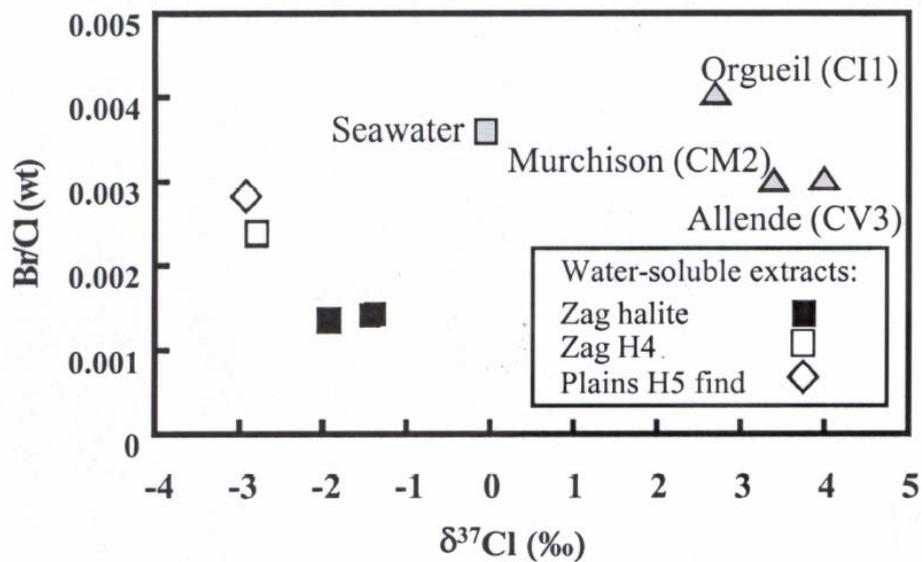


Fig. 3. Br/Cl (wt) vs. $\delta^{37}$Cl (‰). Water soluble extracts (this study): Zag halite (2 samples from 1 grain); Zag (H4 matrix); Plains (H5 find). Terrestrial seawater (Banks et al. 2000). Whole chondrite pyrolysis, Br/Cl ratios and Cl-isotopes for 3 carbonaceous chondrites (Dreibus et al. 1979; Magenheim et al. 1994; 1995).
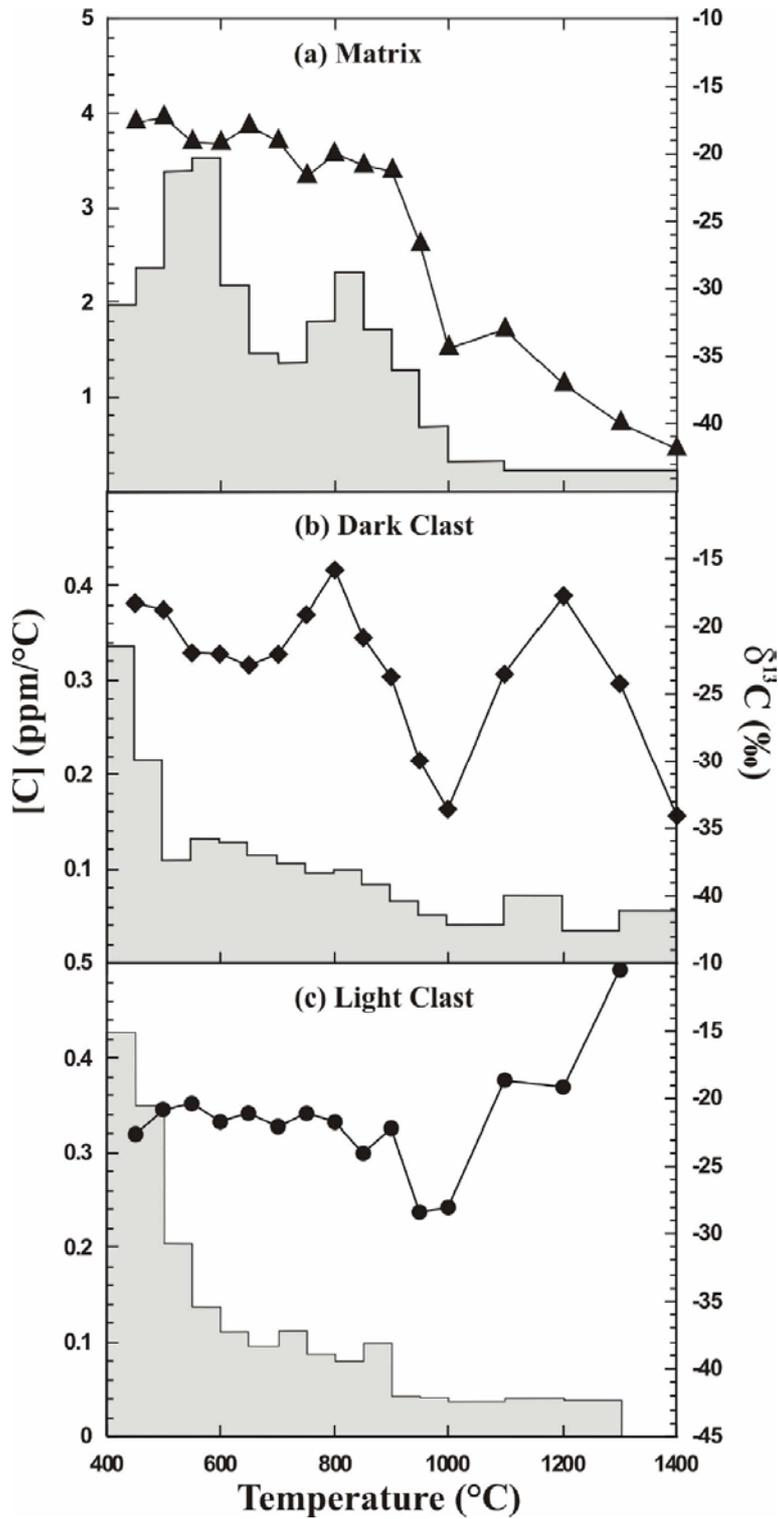
Figure 4. Abundance and isotopic composition of carbon, determined by stepped combustion, in the matrix, dark clast and light clast from Zag. Carbon abundance is plotted as a histogram; isotopic composition given as points. Errors on $\delta^{13}C$ values are the size of the symbols. The carbon released at low temperatures from matrix is $\delta^{13}C$ = -20 ‰, which is consistent with poorly graphitised material being introduced into the matrix rather than indigenous carbonate derived from a brine.