Volatiles in unequilibrated ordinary chondrites: Abundances, sources and implications for explosive volcanism on differentiated asteroids

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Abstract–Keil and Wilson (1993) proposed that, during partial melting of some asteroidal meteorite parent bodies, explosive pyroclastic volcanism accelerated S-rich Fe,Ni-FeS cotectic partial melts into space. These authors argued that this process was responsible for the S-depletion of many of the magmas from which the magmatic iron meteorites formed. This process only requires the presence of a few hundred to thousand ppm of volatiles in asteroids < ~100 km in radius. If the precursor materials of these magmatic iron meteorite groups were similar in composition to unequilibrated ordinary chondrites, then the volatile contents of the latter may be a measure of the potential effectiveness of the process. Analysis of volatile contents of seven unequilibrated ordinary chondrite falls by dynamic high-temperature mass spectrometry revealed that thousands of ppm of indigeneous volatiles, mostly CO, Cl, Na and S, are released at temperatures near the Fe,Ni-FeS cotectic melting temperature of ~980 °C. If these volatiles are largely retained in the asteroidal parent bodies until onset of partial melting, S depletion of the residual melt might have been achieved by ejection of S-rich partial Fe,Ni-FeS melts by pyroclastic volcanism.

INTRODUCTION

As is evidenced by the numerous types of differentiated meteorites in the world's collections, some asteroidal meteorite parent bodies must have experienced complex processes of igneous fractionation and differentiation. Wilson and Keil (1991) drew attention to the fact that many differentiated asteroids may also have experienced explosive volcanism that may have resulted in loss of partial melts as a fine spray (Wilson and Keil, 1994, 1995) into space, if eruption velocities exceeded the escape velocities of the asteroids. Specifically, they suggested that first (basaltic) partial melts explosively erupted from the aubrite parent body and were lost into space 4.55 Ga ago, thus explaining the lack of basaltic (*i.e.*, enstatite-plagioclase) meteorites and clasts from the aubrite parent body. For this mechanism to operate on asteroidal-sized bodies < ~100 km in radius, the basaltic partial melts need only to contain a few hundred to thousand ppm of total volatiles. Muenow *et al.* (1992) measured volatile contents in enstatite chondrites (similar to the likely precursors of the aubrites) and showed that these are sufficient to drive explosive volcanism. This process was also invoked by Warren and Kallemeyn (1992) and Scott *et al.* (1993) to explain the absence of basalts from the ureilite parent body.

Keil and Wilson (1993) suggested that explosive volcanism may also have been responsible for removing even dense Fe,Ni-FeS partial melts, which are negatively buoyant in the absence of volatiles. They argued that removal of these melts can explain the apparent S depletion in igneous iron meteorites, which are fragments of the fractionally crystallized cores of differentiated asteroids. These authors showed that these melts can be driven to asteroidal surfaces because of excess pressure in the melts due to volume expansion as a result of partial melting and due to the presence of buoyant bubbles of gas, which decrease the densities of the melts. They also argued that, as a result of excess pressure in the melts, veins, like those described by McCoy *et al.* (1995) from

acapulcoites, formed, grew into dikes, and served as pathways for migration of melts and gases to asteroidal surfaces. Since cotectic Fe,Ni-FeS melt consists of ~85 wt% FeS and 15 wt% Fe,Ni (Kullerud, 1963; Kubaschewski, 1982), removal of even small volumes of cotectic melt would result in major loss of S but only minor loss of Fe,Ni.

One uncertainty in the Keil and Wilson (1993) proposal is whether the precursor rocks that melted to form differentiated asteroids with metal cores had, in fact, sufficient volatiles to drive Fe,Ni-FeS cotectic melts off the parent bodies by the type of explosive volcanism visualized by these authors. Presumably, these precursor rocks were roughly chondritic in composition, although the specific type of chondritic material is unknown. We explore here whether volatile contents of unequilibrated ordinary chondrites would be sufficient to drive explosive volcanism, if asteroids of such composition were heated to the Fe,Ni-FeS cotectic temperature. If such rocks contained sufficient volatiles, and if some of the igneous iron meteorite groups originated on bodies having similar starting compositions, then it is possible that explosive volcanism may indeed be responsible for the S depletion. We used Knudsen cell mass spectrometry to study seven unequilibrated ordinary chondrite falls. Studies by Gooding and Muenow (1977) of the H6 chondrite Holbrook show that equilibrated chondrites are very low in volatiles, presumably because during metamorphic reheating and subsequent slow cooling, these were lost from the parent body. This places another constraint on the process visualized by Keil and Wilson (1993), namely that some volatiles must be retained within the parent bodies of differentiated asteroids to temperatures at which substantial amounts of partial melt have been produced (*e.g.*, to the melting temperature of the Fe,Ni-FeS cotectic at ~980 °C). Alternatively, the volatiles could have been liberated or produced at or near that temperature, thus providing for the process to be effective.

SAMPLES AND EXPERIMENTAL METHODS

Samples

We analyzed seven unequilibrated ordinary chondrites of different chemical groups (H, L, LL) and petrologic types (3.0–3.7) (Table 1). In an attempt to minimize terrestrial contamination, only observed falls were selected. All samples were fragments (some sawn, some broken) of a few hundred mg and were degassed as received. Samples of Bishunpur (#618.1), Chainpur (#424.1), Khohar (#623.1), Mezö-Madaras (#340.3) and Parnallee (#93sb) were provided by the Center for Meteorite Studies, Arizona State University, and samples of Semarkona and Sharps by the U.S. National Museum, Washington, D.C. Polished thin sections of heated residues of Semarkona (LL3.0; UH 207), Sharps (H3.4; UH 203) and Mezö-Madaras (L3.7; UH 204) were prepared to document changes that occurred during heating and to constrain possible volatile sources. These sections were studied in transmitted and reflected light, and modal analyses were made using the methods of Keil (1962). Each section contains 4–5 slices of the residue, with each slice 2–7 mm in maximum dimension. These sections are preserved in the meteorite collection of the Hawaii Institute of Geophysics and Planetology at the University of Hawaii at Manoa. For comparison, unheated samples of Semarkona (UNM 312) and Mezö-Madaras (UH 52) were also studied. Results of these petrographic studies are not presented here, since they do not substantially contribute to the main theme of this paper.

High-Temperature Mass Spectrometry

The volatile contents of the meteorites were determined using dynamic high-temperature mass spectrometry. Instrumentation consists of an effusion-vaporization source (Knudsen cell), interfaced with a computer-monitored quadrupole mass spectrometer. Details of this facility including calibration, automated data acquisition system and techniques have previously been described (Muenow, 1973; Killingley and Muenow, 1975; Byers *et al.*, 1986). The basic requirement of the high-temperature Knudsen cell mass spectrometer is the production of a beam of molecules representative of the volatiles released from a heated sample and their quantitative mass analysis as a function of temperature. Temperature is measured with a thermocouple secured in the base of the Knudsen cell. The volatiles, after emerging from the effusion cell orifice, are immediately ionized and analyzed by the mass spectrometer. The orifice in the lid of the cell is positioned ~3.8 cm from the ionizer of the mass spectrometer. This configuration virtually eliminates molecular collisions between released volatiles and surfaces; it also permits nearly 100% trans-mission of volatiles to the ionizer. Hence, volatile species measured are identical to those that are actually released from the samples. A shutter-plate located between the orifice and ionizer can be used to distinguish volatiles being released from the heated sample from those due to background contributions.

In a typical degassing study, the mass spectrometer is operated in a rapid scan mode to obtain mass pyrograms. Samples (typically 5 to 6 fragments with a total mass of ~60–90 mg) are loaded into a pre-baked, high purity Al oxide cell liner and degassed by heating at 5 °C/min to ~1300 °C under a vacuum of 10^{-7} to 10^{-8} torr. This rate was selected because, for the relatively low volatile contents of chondrites, it provides the optimal signal to background ratio, thus allowing us to determine volatile abundances at higher accuracies than if we had used a lower rate of heating with commensurately lower signal to background ratio. In any case, it is, of course, impossible to duplicate in the laboratory the actual slow heating (and cooling) rates experienced by asteroids, and the experimental rate is thus orders of magnitude faster. However, we are mainly concerned with determining the volatile species, their abundances, and release temperatures, which our past experience in this laboratory (unpublished data) shows can be accurately determined with this heating rate. During the entire degassing period, the mass spectrometer rapidly scans the spectrum from 2 to ~100 atomic mass units. Ion-current signals for all mass peaks and temperature are measured (using an IBM PC/AT computer) and stored on a hard disk for later data reduction. Mass pyrograms were obtained as plots of the intensities of parent molecular ions (or principal fragment ions) *vs.* temperature. For example, for the volatile CO_2, one typically plots the parent mass peak m/e = 44 *vs.* temperature, rather than the fragment peak at m/e = 28 (CO^+), which could also be the parent peak for N_2^+ and/or CO. In cases where more than one species can share the same observed m/e values (*e.g.*, N_2^+, CO^+ at m/e = 28), appearance potential measurements were made to distinguish among possible neutral molecular precursors (Grimley, 1967). These measured intensities are proportional to partial pressures of the various volatiles released from the sample. Mass pyrograms permit the quantitative characterization of sample volatility, since the area under each curve, when corrected for isotopic abundance, fragmentation effects and

other molecular parameters, is proportional to the total amount of each volatile being released. System background contributions were determined from "blank" runs made after each sample study. When degassing is completed, the sample is cooled and reweighed. Analytical uncertainties (based on reproducibility of these samples) are: H_2O, ± 200 ppm; CO, CO_2, hydrocarbons, ± 100 ppm; Cl, Na, S, ±50 ppm.

VOLATILE ABUNDANCES AND RELEASE TEMPERATURES

The mass pyrograms obtained from Chainpur showing the release of principal volatiles, H_2O, CO, CO_2, CH_4, C_2H_6, S_2, Cl and Na from 100–1300 °C are shown in Fig. 1. These species are observed either as parent ions or their more abundant ion fragments. All seven meteorites studied exhibit release patterns similar to that of Chainpur, with some variation in the onset temperatures, especially for the release of CO (800–950 °C) and Cl (750–1000 °C). Intensities and, hence, abundances of individual volatile species are different for each meteorite.

Volatile abundances for CO, CO_2, and Cl are summarized in Table 1. Abundances for H_2O are highly variable and range from ~1500 to 7500 ppm, in agreement with values found previously for enstatite chondrites (Muenow *et al.*, 1992). Water in all chondrites except Semarkona was released <600 °C. Reliable abundances for CH_4, C_2H_6 and other numerous low-molecular weight hydrocarbons could not be obtained due to their low intensities and complex fragmentation patterns. All of these are released at low temperatures (<600 °C). Carbon dioxide is released from all meteorites at ~750 °C. Two meteorites, Semarkona and Bishunpur, also show small releases of CO_2 between 1100 and 1200 °C.

Due to a 1300 °C upper temperature operating limit of the mass spectrometer, not all of the S and Cl could be released from the samples (see Fig. 1). Accordingly, S abundances are not reported;

TABLE 1. Abundances and on-set release temperatures of some volatiles released from ordinary chondrites between 750 and 1300 °C during vacuum pyrolysis.

Meteorite	CO (ppm)	CO_2 (ppm)	Cl (ppm)[+]	Total C (wt%)* (this study)	Total C (wt%)[†] (literature)
Semarkona LL3.0	3480 (800 °C)	425 (750 °C)	380 (835 °C)	0.161	0.538(a)
Bishunpur LL3.1	3880 (825 °C)	480 (750 °C)	455 (800 °C)	0.179	0.433(a)
Chainpur LL3.4	1640 (900 °C)	160 (775 °C)	450 (800 °C)	0.074	0.304(a)
Sharps H3.4	8550 (800 °C)	400 (770 °C)	440 (750 °C)	0.377	1.77(a)
Khohar L3.6	2740 (900 °C)	400 (770 °C)	445 (950 °C)	0.128	0.365(a)
Parnallee LL3.6	245 (900 °C)	50 (800 °C)	450 (1000 °C)	0.012	0.120(b)
Mezö-Madaras L3.7	1250 (950 °C)	320 (800 °C)	415 (850 °C)	0.063	0.193(a)

* Does not include low-temperature (<600 °C) contaminant hydrocarbon contribution or that portion of graphitic-carbon not released as CO during vacuum pyrolysis.
† Stepped combustion in O_2 followed by mass spectrometric analysis.
+ Minimum values since not all Cl is released by 1300 °C (see Fig. 1).
(a) Grady *et al.*, 1989.
(b) Grady *et al.*, 1982.

those for Cl, however, even though they represent minimum values, are presented in Table 1, because Cl abundances have not been previously reported for these meteorites. The temperature of the onset of Cl release varies from 750 to 1000 °C. The release envelope for Chainpur is bi-modal (Fig. 1), indicating at least two sources of Cl. For all the meteorites, small amounts of Na vapor begin to be released at ~1000 °C.

DISCUSSION

Sources of Volatiles

Here, we attempt to identify the host phases of the volatiles, using petrographic, mineralogic and release temperature considerations as guides. This is a difficult undertaking, and our findings are subject to considerable uncertainties. As one would expect, most, but not all, of the host phases for these volatiles appear to be contained in the matrices of the chondrites, rather than in the more refractory chondrules. The matrices are composed dominantly of

mafic silicates, feldspathic materials, opaques and organic and graphitic C (Scott *et al.*, 1988a). Several of the unequilibrated ordinary chondrites have also experienced significant aqueous alteration on their parent bodies (Hutchison *et al.*, 1987; Guimon *et al.*, 1988; Alexander *et al.*, 1989a), as is evidenced by the presence of smectite (*e.g.*, Semarkona, Bishunpur) and other products of Cl-alkaline-H_2O metasomatism (*e.g.*, Sharps, Bishunpur, Parnallee) (Alexander *et al.*, 1994). This diverse mineralogy (*e.g.*, Krot *et al.*, 1995) and possibilities for terrestrial contamination are the main reasons for the uncertainties in our attempts to identify potential host phases.

Contaminant Volatiles–Water, low-molecular weight hydro-carbons and CO_2 appear to derive principally from terrestrial sources and are considered contaminants.

Water (m/e = 18) is released in large abundances between ~150 and 500 °C. It appears likely that much of this water is physically adsorbed, as also noted for enstatite chondrites (Muenow *et al.*,
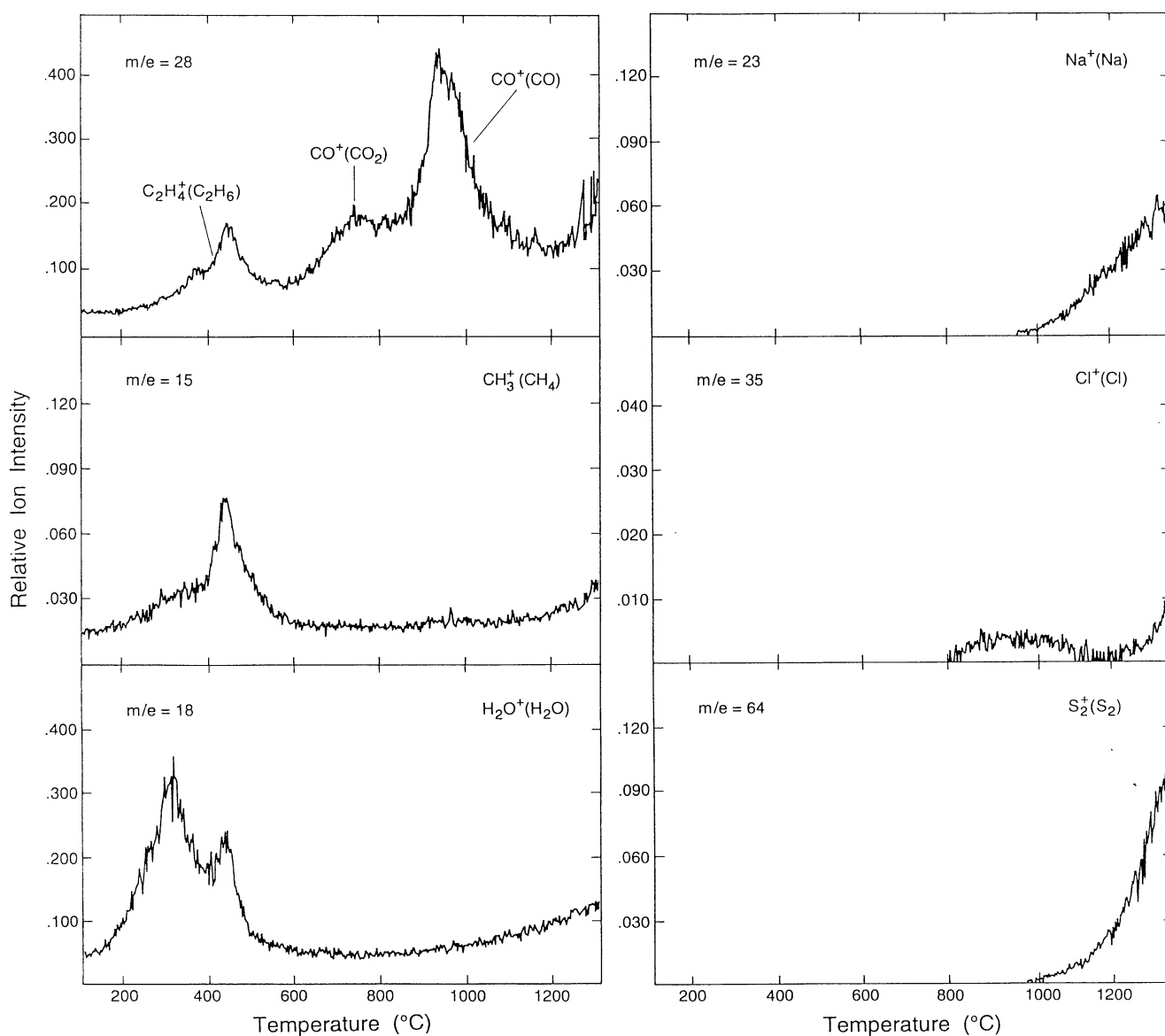

FIG. 1. Mass pyrogram for Chainpur showing release of principal volatiles from 100–1300 °C (background uncorrected). Ionic species are those detected; species in parentheses are their neutral molecular precursors. Heating rate is 5°/min. Note differences in vertical scale.

1992). A small portion might also come from terrestrial weathering products of metallic Fe,Ni. Decomposition of "rust" minerals such as goethite (FeOOH) releases H_2O at low temperatures (150–650 °C) and CO at higher temperatures (900–1200 °C) when the Fe, Ni and Co oxides react with C. While we would expect such weathering products to be minimal in observed falls, some of these meteorites have had extensive terrestrial residence periods (all seven meteorites fell between 1852 and 1940). Finally, it is likely that some portion of the water is indigenous in some specimens. Alexander *et al.* (1989a) documented the almost complete conversion of the matrix of Semarkona to a hydrated smectite. Decomposition of this smectite upon heating would release substantial amounts of water, consistent with the observation of an additional higher-temperature (600–750 °C) release peak of ~250 ppm H_2O for Semarkona. Smectite was also observed by Alexander *et al.* (1989a) in Bishunpur (LL3.1) but in much smaller abundances. We did not observe a higher-temperature H_2O component in Bishunpur, possibly due to sample heterogeneities.

Low-molecular weight hydrocarbons (*e.g.*, m/e = 15), released at temperatures <600 °C, are likely to be contaminants in these samples. Muenow *et al.* (1992) observed similar species in enstatite chondrites and attributed them to contamination from fluids used during cutting and other handling prior to receipt of the samples. Previous studies of ordinary chondrites (Grady *et al.*, 1989) have shown that C released at low temperatures during stepped-combustion gas extraction procedures is isotopically light, which argues for weathering/contaminant sources for these hydrocarbons. However, a small amount may be released by decomposition of indigeneous "organic" components, such as those described for a number of unequilibrated ordinary chondrites by Alexander *et al.* (1990).

Carbon dioxide (m/e = 44) is predominantly released at ~750 °C in all meteorites studied. In Fig. 1, its release behavior is given by its principal fragment ion CO^+ at m/e = 28. The most likely source of CO_2, judging from the release temperature, is the decomposition of carbonates, such as calcite ($CaCO_3$). However, we are unsure of the precise origin of this carbonate. In the lowest petrologic subtype chondrites, some of the carbonates are probably indigenous. For example, Alexander *et al.* (1989a) identified minor amounts of calcite in the matrix of Semarkona and conclude that it probably formed by aqueous alteration on the parent body. This amount must, however, be minor, since Semarkona does not exhibit higher CO_2 abundances than the other unequilibrated ordinary chondrites studied here in which no indigenous carbonates have been reported. Since all chondrites studied here exhibit similar CO_2-release patterns to that of Semarkona, we suggest that at least some of the carbonate must be of terrestrial origin. While this would appear surprising in observed falls, these meteorites have experienced long terrestrial residence periods in museums, often with no humidity control, and carbonates have been observed in a number of ordinary chondrite finds (*e.g.*, Velbel *et al.*, 1991). It should also be noted that the CO_2 abundances observed (50–480 ppm) correspond to only 0.01–0.11 wt% $CaCO_3$. We also observed small releases of CO_2 between 1100 and 1200 °C in Semarkona and Bishunpur. While the source of this CO_2 remains uncertain, one possibility is the mineral scapolite, which has been identified in Bishunpur (Alexander *et al.*, 1987) and has a large CO_2 release ~1100 °C (this laboratory; unpublished data).

Indigenous Volatiles–Four of the observed volatile species (CO, Cl, Na, S_2) are released at high temperatures. We suggest that

these volatiles are derived from host phases indigenous to the meteorites.

Carbon monoxide (m/e = 28) deserves special note, since it is the major volatile released at ~950 °C, the temperature of Fe,Ni-FeS cotectic melting in a chondritic system. In a previous degassing study of seven enstatite chondrites, Muenow *et al.* (1992) found that substantial amounts of CO (1580–2830 ppm) were released in a narrow temperature interval beginning at ~1025 °C. They suggested that possible sites for CO include microscopic vesicles, small inclusions within silicates, and adsorbates trapped along intergrain microcracks. This conclusion was based in part on the sudden and violent burst-release behavior of CO over a narrow temperature interval, the highly vesiculated and pitted nature of the samples as observed after heating and the presence of numerous tiny spherules of metallic Fe,Ni and Fe,Ni-FeS mixtures observed on the inner walls of the sample crucible after heating, which were explosively ejected from the sample. An alternative origin for the CO, which Muenow *et al.* (1992) considered, is a reduction reaction during pyrolysis of enstatite chondrites with C reacting with a minor amount of Fs component in pyroxene to form CO. However, the violent and sudden burst-release behavior of CO over a narrow temperature range and the low amounts of Fs in the highly reduced enstatite chondrites render this latter explanation unlikely (Muenow *et al.*, 1992).

However, the release of CO from submicroscopic vesicles or inclusions in the ordinary chondrites studied here does not seem reasonable, based principally on two observations: (1) the CO release envelope for the ordinary chondrites is broad, extending over a 200–250 °C temperature interval with no "burst-release spikes" observed in either the mass pyrograms or with the oscilloscope of the mass spectrometer; and (2) the total lack of tiny spherules of metal and sulfide deposited uniformly on the inner walls of the crucible, again indicating no burst-release of trapped gas.

Therefore, several other potential sources for CO release have been considered. The first is the breakdown of "rust" minerals, such as goethite (FeOOH). As noted earlier, terrestrial weathering products of metallic Fe,Ni and FeS would release H_2O at low temperatures during dehydration, followed by CO at higher temperatures as a result of decomposition of Fe, Ni- and Co-oxides and reaction with indigenous C. Although it is probable that some weathering products occur even in these observed falls, the amounts of weathering products and their contributions to the total production of CO are probably small.

A second source might be the decomposition of indigenous Fe oxides and reaction with graphite. Such oxides are maghemite (γ-Fe_2O_3), identified by Alexander *et al.* (1989a) in the matrix of Semarkona, magnetite (Fe_3O_4) in Semarkona, and graphite-magnetite aggregates in a number of unequilibrated ordinary chondrites (*e.g.*, McKinley *et al.*, 1981; Scott *et al.*, 1981; Brearley *et al.*, 1987; Brearley, 1990). However, Semarkona does not show appreciably greater amounts of CO than the other meteorites studied, and, thus, this reaction probably does not contribute a major amount of the CO observed.

A third possibility is that the CO is produced during pyrolysis by reaction of indigenous graphite with the FeO in the silicates of the matrices of the unequilibrated ordinary chondrites (*e.g.*, $FeMgSiO_4 + C = MgSiO_3 + Fe + CO$; $FeSiO_3 + C = SiO_2 + Fe + CO$). This reaction has previously been invoked to account for reduction processes believed to have occurred on the parent body of

the ureilites (Warren and Kallemeyn, 1992) and during meta-morphism on some ordinary and carbonaceous chondrite bodies (Wasson *et al.,* 1993; Lee *et al.,* 1992). Although highly pressure sensitive (reactants being favored with increasing pressure), Walker and Grove (1993) demonstrated in an experimental high-pressure study that reduction of silicates with graphite to yield metallic Fe and CO gas can indeed occur significantly at pressures <100 bars (equivalent to that expected at the center of a 100 km radius asteroid). Since there is no reason to suggest that the parent bodies of the magmatic iron meteorites were any larger than this, the reaction discussed above is likely to be responsible for the CO not only in our experiments but also in differentiated asteroid. The meteorite Semarkona is a special case among the unequilibrated ordinary chondrites studied here in that it does not contain graphite but instead contains carbides (*e.g.,* Taylor *et al.,* 1981). These are thought to have formed by parent-body alteration of metallic Fe,Ni by C-O-H fluids (*e.g.,* Krot *et al.,* 1995). Furthermore, in Semarkona, FeO-rich olivine has been altered to FeO-rich phyllosilicates such as smectite (Hutchison *et al.,* 1987). Since the CO release of Semarkona (not shown in Fig. 1) is essentially identical to that of Chainpur, it appears that during pyrolysis, the unstable carbides break down to graphite, which reacts with the break-down products of the FeO-rich smectite to form metallic Fe and CO.

In order to test the hypothesis that reduction reactions as noted above may be important in the present degassing experiments, we mixed equal volumes of finely ground San Carlos, Arizona, olivine, and spectroscopically pure graphite. The olivine was carefully selected to avoid any optically visible inclusions. The powdered samples were then ground together with a small amount of distilled water to form a paste, which was then pressed into a pellet. After drying in an oven at 150 °C for 24 h, a 100-mg section of the pellet was placed into a previously baked-out crucible and degassed in the same mass spectrometer and under the same conditions that were employed in the analysis of the ordinary chondrites; the experiment was carried out with two separate pellets with essentially the same results. Copious amounts of CO were produced beginning at ~1000 °C (Fig. 2), a temperature higher than that for the chondrites (800–950 °C; Fig. 1). We suggest that this difference is probably the result of significant differences in precise mineralogy and grain size between the chondrites and the experimental charges (meteorites contain pyroxene as well as olivine; FeO content in matrix olivine of unequilibrated ordinary chondrites is much higher than in San Carlos olivine, which is Fa_{8-11}; C may in part be poorly-graphitized or amorphous in the chondrites, whereas it is well-crystalline in the experimental charges; grain size is probably smaller for the meteorites and grain intergrowth more intimate than in the experimental charges). To further examine our model, polished thin sections were prepared of the heated and unheated mixtures, and in neither section was metallic Fe detected by optical microscopy. A second heated charge was studied by Mössbauer spectroscopy, and no metallic Fe was detected. However, upon careful examination of the Knudsen cell of the mass spectrometer, a thin silver-gray coating was observed on the inner surface of the lid of the crucible. Subsequent analysis of this film by atomic absorption spectrometry shows it to consist of Fe and, based on its optical appearance, of metallic Fe. Apparently, the metallic Fe produced in the reduction reaction during heating was vaporized during the experiment and trapped on this part of the crucible, which, at high temperatures, is cooler than the rest of the crucible, thus acting as a cold trap.
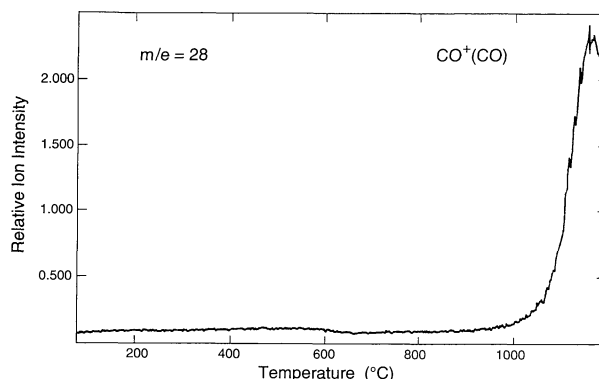

FIG. 2. Mass pyrogram of San Carlos olivine-graphite mixture showing release of CO beginning at ~1000 °C. A similar reaction between indigeneous C and FeO-rich olivine in the matrix of the heated chondrites produces the CO observed.

Closer examination of the CO abundances of the seven unequilibrated ordinary chondrites studied reveals some interesting features. The most notable of these is the very high CO abundance in Sharps (8550 ppm; Table 1). This is more than twice that of any other meteorite studied. Sharps is known to contain abundant C-rich aggregates (Scott *et al.,* 1988b), and this abundant supply of C could be the cause for the abundant CO release by this chondrite. A second interesting feature of the data is that the higher petrologic subtypes (3.4–3.7, with the exception of Sharps) tend to release less CO than the lower petrologic subtypes (3.0–3.1), apparently because they contain less C and FeO in their matrices. While considerable scatter exists in this data set, this general observation is at least consistent with expectations. Grady *et al.* (1982) documented that total C abundances tend to decrease with increasing petrologic type, and Huss *et al.* (1981) and Nagahara (1984) showed that the FeO contents of matrix olivines tend to decrease with increasing petrologic type. Finally, it is interesting to note that the total C contents obtained in this study from the measured CO contents are consistently lower, up to an order of magnitude, than C contents measured by stepped combustion in O followed by mass spectrometric analysis (Table 1). This suggests that not all of the C has reacted with FeO-rich silicates to form CO in our experiments. In the stepped combustion experiments, introduced O allows combustion and removal of all C.

Chlorine (m/e = 35, 37) starts to be released at temperatures of 750–1000 °C in these meteorites. It is monitored as mass peak m/e = 35 rather than its less abundant isotope at m/e = 37. The release is incomplete, due to the 1300 °C upper limit operating temperature of the mass spectrometer. Chainpur exhibits a bi-modal release envelope for Cl (Fig. 1), suggesting that there are at least two sources of Cl in this meteorite. One possible source of the incomplete high-temperature release in the low petrologic subtype chondrites (which have been aqueously altered), is scapolite. As noted earlier, decomposition of scapolite will release both CO_2 and Cl at ~1100 °C. In both Semarkona and Bishunpur, small release peaks of CO_2 are noted at this temperature, suggesting that scapolite may be decomposing. Several of the other unequilibrated ordinary chondrites studied here also exhibit petrologic and/or chemical evidence for Cl ± H_2O-metasomatism. These include Sharps (Alexander *et al.,* 1989b), Chainpur (Alexander *et al.,* 1994) and Parnallee (Kennedy *et al.,* 1992). We do not, however, suggest that

these alteration products are the major source of Cl release in these meteorites. Evidence against this include the very small release of high-temperature CO_2 from Semarkona and Bishunpur, which should accompany release of Cl from scapolite, and the release of large amounts of Cl from meteorites, which show no evidence of metasomatism. We suggest that most of the observed Cl results from Cl dissolved in silicate glass in chondrules in the low petrologic type chondrites and from the decomposition of chlorapatite in the higher petrologic types. It is known that terrestrial volcanic glassy basalts have typical Cl abundances of 10–1000 ppm, which is released from ~900–1200 °C (Michael and Schilling, 1989), not unlike what is observed in the meteorites studied here. In addition, studies of acapulcoites (McCoy *et al.*, 1995) suggest that phosphates (both whitlockite and apatite) melt at the Fe,Ni-FeS cotectic. This is consistent with the onset temperature of the Cl release, which is close to the melting point of the Fe,Ni-FeS cotectic.

Sodium (m/e = 23) is released in small amounts beginning at ~1000 °C for all meteorites. Release is incomplete at the 1300 °C upper temperature operating limit. It is almost certain that it results from the decomposition of sodic feldspar or glassy, feldsathic chondrule mesostases. The onset temperature of Na release (~1050 °C) is consistent with the melting temperature of pyroxene-plagioclase as the first silicate melt in a chondritic system.

Sulfur (m/e = 64) is released as S_2 starting at ~1000° C. Release is incomplete at the 1300 °C upper temperature operating limit. It clearly results from the decomposition of troilite (FeS), which melts in contact with Fe,Ni metal at the ~980 °C cotectic temperature.

Implications for Explosive Volcanism on Differentiated Asteroids

Our experiments indicate that during heating and partial melting of unequilibrated ordinary chondrites, thousands of ppm of indigeneous volatiles are released at temperatures near the Fe,Ni-FeS cotectic of ~980 °C. Thus, if the precursor materials to differentiated asteroids, which formed fractionally crystallized Fe,Ni cores, had been similar to ordinary chondrites, then sufficient volatiles would have been released to drive the type of pyroclastic volcanism envisioned by Keil and Wilson (1993). This process entails internal heating followed by expulsion of the first cotectic Fe,Ni-FeS partial melts that, because of the high (85 wt%) proportion of FeS in these melts, would result in depletion of S in the fractionally crystallizing metal cores and, thus, explain the S depletion observed in many of the magmatic iron meteorites. The fact that the major volatile species, CO, may not be present as a trapped gas but probably results from the reaction of C with FeO present in the mafic silicates is consistent with the model, since our experiments show that this reaction takes place near the Fe,Ni-FeS cotectic temperature.

In order for partial melts to be explosively removed from the parent body, some of the volatiles must have either been retained in the body to temperatures where partial melting sets in, or been liberated and/or produced at those temperatures (such as the CO mentioned above). We speculate that this was the case on the aubrite (Wilson and Keil, 1991; Muenow *et al.*, 1992) and the ureilite (Warren and Kallemeyn, 1992; Scott *et al.*, 1993) parent bodies, where plagioclase-pyroxene (*i.e.*, basaltic) partial melts appear to have been removed. We also speculate that this was the case for the parent bodies of those magmatic iron meteorite groups whose metal magmas appear to have been depleted in S.

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