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The chlorine isotope composition of chondrites : evidence for a single nebular reservoir and the effects of secondary processes on chondrite parent bodies

Jessica Mumphrey

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**THE CHLORINE ISOTOPE COMPOSITION OF
CHONDRITES: EVIDENCE FOR A SINGLE NEBULAR
RESERVOIR AND THE EFFECTS OF SECONDARY
PROCESSES ON CHONDRITE PARENT BODIES**

by

JESSICA A. MUMPHREY

B.S., GEOLOGY, LOUISIANA STATE UNIVERSITY, 2009

THESIS

Submitted in Partial Fulfillment of the
Requirements for the Degree of

Master of Science

Earth and Planetary Science

The University of New Mexico
Albuquerque, New Mexico

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ABSTRACT

The chlorine isotope composition of chondrites provides information about isotopic reservoirs that were present in the solar nebula and the effect of secondary processes on the isotopic composition. We analyzed twenty chondrites that included both unaltered (type 3) and altered (types 1-2, 4-6) chondrites from the carbonaceous, ordinary, and enstatite classes. Petrologic type 3 chondrites are the least equilibrated and are those most likely to retain primary nebular signatures. By analyzing unaltered, pristine, chondrites from each class, we can determine if chlorine isotope variations existed among the classes and thus if multiple isotopic reservoirs existed. Since chlorine behaves as a hydrophile and volatile element, analyses of aqueously altered (types 1-2) and metamorphosed (types 4-6) chondrites provide insight into effects of secondary processes on the chlorine isotope composition.

Type 3 chondrites have similar $\delta^{37}\text{Cl}$ values that average $-0.3 \pm 0.4\%$. This value is indistinguishable from the $\delta^{37}\text{Cl}$ values of the bulk Earth, lowest measured value of the Moon, and the average of martian meteorite samples from the literature. From this

similarity, we conclude that the inner regions of the solar nebula had a homogeneous chlorine isotope reservoir. For samples that have undergone secondary processing, we observe slight variations from -2.1 to 1.0‰ for metamorphosed samples (average -0.3‰) and -2.0 to 2.7‰ for aqueously altered samples (average 0.7‰). We conclude that these processes were not significant in fractionating the chlorine isotopes.

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1: INTRODUCTION

The chlorine isotope values of chondritic meteorites may contribute to understanding the distribution of chlorine isotope reservoirs in the solar nebula as well as provide insights into the processes experienced by the meteorite. The primary focus of this study is the chlorine isotope composition of chondritic meteorites since chondrites record information about early solar system processes including condensation, evaporation, chondrule formation, aqueous alteration, and thermal metamorphism. The initial chlorine isotope compositions of chondrites are useful in understanding the variability of chlorine isotopes in the early solar nebula. The initial chlorine isotope compositions can also help decipher the initial chlorine isotope composition of planetary bodies, such as Earth. Chlorine is a volatile and hydrophile element (Sharp et al., 2010a); therefore, processes such as metamorphism and aqueous alteration that occurred on the chondrite parent body can change the chlorine abundance and possibly fractionate the chlorine isotopes.

Previous studies of the chlorine isotope composition of chondrites have not agreed on $\delta^{37}\text{Cl}$ values (Fig. 1). Magenheimer et al. (1995) analyzed bulk carbonaceous chondrites using thermal ionization mass spectrometry (TIMS) and reported positive $\delta^{37}\text{Cl}$ values from 2.6 to 4‰. Nakamura et al. (2007) also used TIMS and measured several bulk chondrites from various classes. They found large variations with ranges of -4.6 to +5.0‰ for ordinary chondrites, -0.6 to +4.4‰ for carbonaceous chondrites, and +3.0 to +5.2‰ for enstatite chondrites. Nakamura et al. (2007) attributed the variation in $\delta^{37}\text{Cl}$ values to multiple isotopic reservoirs in the solar nebula and secondary processing on a parent body. In contrast to these studies using TIMS analysis, Sharp et al. (2007) analyzed

carbonaceous chondrites using gas source isotope ratio mass spectrometry (IRMS) and obtained a more limited range of $\delta^{37}\text{Cl}$ values, between -0.7 and 1.2‰. It was difficult to reconcile the different results from the two techniques. Several authors using IRMS for measuring the $\delta^{37}\text{Cl}$ values of terrestrial materials concluded that data obtained by TIMS were not reliable due to analytical errors (Bonifacie et al., 2008; Sharp and Barnes, 2008). More recently, Nakamura et al. (2011) refined the TIMS method and suggested that the previous values determined by TIMS were not reliable due to problems with the analytical technique.

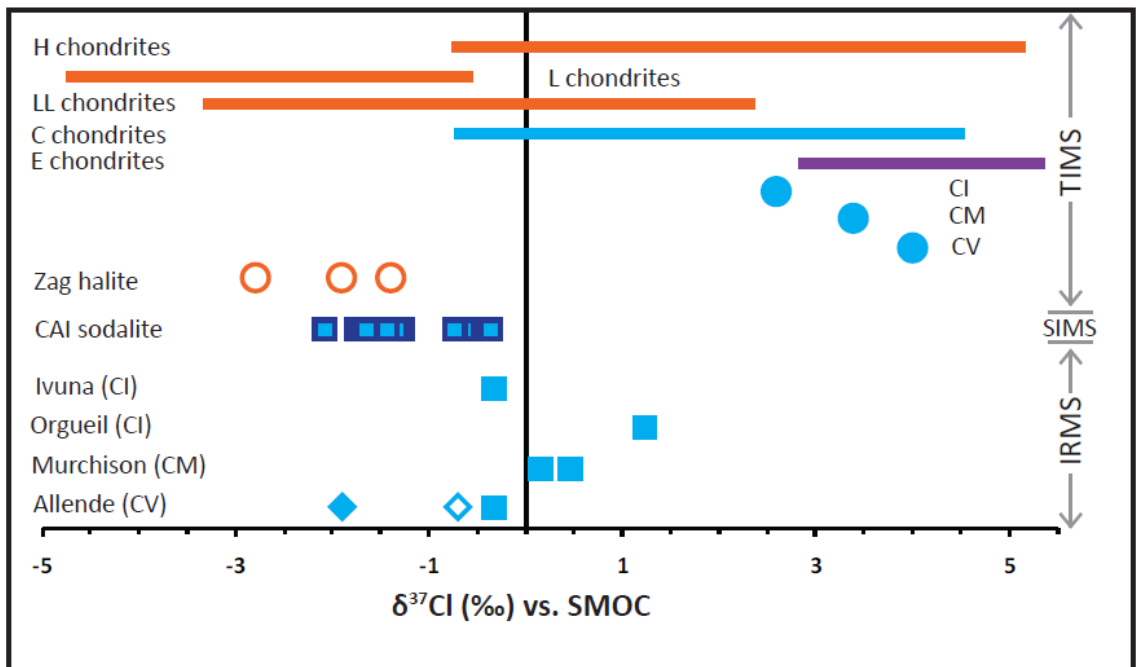


Figure 1: $\delta^{37}\text{Cl}$ values of bulk chondritic meteorites from previous research. Ordinary chondrites are in orange, carbonaceous chondrites in blue, and enstatite chondrites in purple. Data are divided according to the analytical method used for measuring $\delta^{37}\text{Cl}$: thermal ionization mass spectrometry (TIMS), secondary ion mass spectrometry (SIMS), and gas source isotope ratio mass spectrometry (IRMS). TIMS data are from the following: solid lines (Nakamura et al., 2007), filled circles (Magenheim et al., 1995), and open circles (Bridges et al., 2004). Zag halites (open circles) are from an H ordinary chondrite. Squares represent analyses by Sharp et al. (2007). Blue squares with blue outline are individual analyses of sodalite grains in an Allende (CV) CAI from Sharp et al. (2007). Diamonds represent analyses by Bonifacie et al. (2007). Unfilled symbols represent soluble Cl (WSC/leachate) and filled symbols represent bulk measurements.

In this study, we determined the chlorine isotope values of a wide range of chondrites, since previous values only include a few carbonaceous chondrites analyzed by Sharp et al. (2007) and the potentially erroneous TIMS data. This study also expands on previous work by analyzing both structurally-bound chloride (SBC) and water-soluble chloride (WSC) for each meteorite. Our study includes chondrite falls from a range of petrologic types including types 1 through 4 for the carbonaceous (C) class, types 3 through 6 for the ordinary (O) class, and types 3 through 7 for the enstatite (E) class. Observed chondrite falls are less likely than finds to have experienced terrestrial contamination and are treated as a more reliable source of information about the nebula and secondary processes on chondrite parent bodies.

The first goal of the study is to determine whether the solar nebula had a homogeneous or heterogeneous chlorine isotope composition by analyzing the least altered chondrites. Petrologic type 3 chondrites are the most unequilibrated chondrites, have undergone the least amount of secondary processing (Van Schmus and Wood, 1967), and are therefore most likely to retain initial nebular signatures. Although some research has been done previously on the chlorine isotope composition of chondrites (Magenheim et al, 1995; Nakamura et al., 2007; Bonifacie et al., 2007; Sharp et al., 2007), none has focused on the $\delta^{37}\text{Cl}$ values of type 3 chondrites from the different chondrite classes.

The second goal of the study is to investigate the effect of metamorphism and aqueous alteration on chlorine concentration and chlorine isotope composition by analyzing altered chondrites. In altered samples, a low Cl abundance relative to type 3 abundances may indicate Cl^- loss during metamorphism or leaching during aqueous

alteration. However, aqueous alteration could also introduce Cl into a chondrite and precipitate Cl-bearing phases, thereby raising the Cl concentration. Aqueous alteration may also redistribute chlorine within a sample as well. Fractionation of Cl isotopes may occur during these processes. The $\delta^{37}\text{Cl}$ values of the least altered (type 3) chondrites provide benchmarks from which to evaluate isotope fractionation resulting from secondary processes. However, little is known about how chlorine fractionates during secondary processes on chondrite parent bodies. In addition, the presence or absence of a fluid during metamorphism and the presence or absence of relatively high temperatures (greater than 300°C) during aqueous alteration could change the isotopic fractionations that we would assume occurred.

The third goal of this work is to determine the relationship between the SBC and WSC $\delta^{37}\text{Cl}$ values, which represent different host mineral phases for Cl, and the $\delta^{37}\text{Cl}$ value of individual Cl-bearing phases in chondrites by analyzing several Cl-bearing phases *in situ* by secondary ion mass spectrometry (SIMS).

Overall, in this study we hope to establish $\delta^{37}\text{Cl}$ values for a wide range of chondrites in order to improve our understanding of the reservoirs of Cl isotopes in the early solar system and the processes that may have fractionated Cl isotopes during alteration and metamorphism on chondrite parent bodies.

2: SAMPLES & ANALYTICAL TECHNIQUES

Bulk Analyses

We analyzed eight carbonaceous (C) chondrites, seven ordinary (O) chondrites, and five enstatite (E) chondrites. Table 1 lists the bulk samples analyzed as well as the chondrite class and group of the sample, petrologic type, whether the sample is a fall or find, and the source of the sample. Most samples were obtained from the collection of the Institute of Meteoritics (IOM) at the University of New Mexico (UNM). Saint-Séverin was obtained from the Muséum national d'Histoire naturelle (MNHN, Paris). The Qingzhen sample was obtained from Alan Rubin and John Wasson of the University of California Los Angeles (UCLA).

Table 1: List of bulk chondrite samples analyzed in this study.

	Group	Petrologic Type	Fall or Find	Source
Carbonaceous Chondrites				
Orgueil	CI	1	Fall	UNM-IOM
Murray	CM	2	Fall	UNM-IOM
NWA6216	CR	2	Find	M. Tyra
Allende	CV	3	Fall	UNM-IOM
Vigarano	CV	3	Fall	UNM-IOM
Kainsaz	CO	3.2	Fall	UNM-IOM
Ornans	CO	3.4	Fall	UNM-IOM
Karoonda	CK	4	Fall	UNM-IOM
Ordinary Chondrites				
Parnallee	LL	3.6	Fall	UNM-IOM
Dhajala	H	3.8	Fall	UNM-IOM
Zag	H	3-6	Fall	UNM-IOM
Bjurböle	L/LL	4	Fall	UNM-IOM
Tuxtuac	LL	5	Fall	UNM-IOM
Sulagiri	LL	6	Fall	UNM-IOM
Saint-Séverin	LL	6	Fall	MNHN
Enstatite Chondrites				
Qingzhen	EH	3	Fall	UCLA
Abee	EH	4	Fall	UNM-IOM
Itqiy	EH	7	Fall	UNM-IOM
Eagle	EL	6	Fall	UNM-IOM
Yilmia	EL	6	Find	UNM-IOM

Each sample, about 200 mg to 1 g of material, was first rinsed with 18 M Ω deionized water to clean the surface of contamination. If enough sample material was available, duplicates or triplicates of the same chondrite were analyzed in order to improve precision. Samples were then crushed to a fine powder in a dry mortar and pestle. The powder was leached with 18 M Ω deionized water and sonicated to remove any water soluble chloride from the sample. Chlorine was recovered from the rock powders using a pyrohydrolysis method by melting the powdered sample in a water vapor stream and then condensing the water vapor (Magenheim et al., 1994). Aqueous Cl⁻ from both the leachate (WSC) and the rock-derived chloride (SBC) was converted to AgCl and ultimately CH₃Cl gas using a modified procedure from Eggenkamp (1994). The modified procedure includes the addition of 10 mL of 50% nitric acid to the solution before conversion to AgCl. Nitric acid is added to remove any sulfur present in the solution (Barnes et al., 2009). CH₃Cl gas was analyzed in the ThermoQuest Finnigan DeltaPlusXL mass spectrometer at UNM using the continuous flow method as described by Sharp et al. (2007). During continuous flow analyses, the area (time • voltage) and the voltage of the sample and standards were recorded in addition to the $\delta^{37}\text{Cl}$ value. The signal strength as inferred from the area is then used as an indicator of sample size. The known Cl concentration of the standard combined with the area and voltage of the standard could then be used to calculate the Cl concentration of the sample. Analyses with areas less than 200 millivolts • sec were discarded and considered unreliable because of low Cl concentration. In the case of Itqiy, although both duplicates were below 200 millivolts • s and do not pass our criteria for high-quality analyses, the results were reproducible, so we do report these values.

Chlorine isotope compositions are reported in the standard delta notation, given by $\delta^{37}\text{Cl} = \left(\frac{{}^{37}\text{Cl}}{{}^{35}\text{Cl}}_{\text{sample}} / \frac{{}^{37}\text{Cl}}{{}^{35}\text{Cl}}_{\text{std}} - 1 \right) \times 1000$. Data are reported relative to Standard Mean Ocean Chloride (SMOC), which by definition has a delta value of 0‰.

Standardization is relative to seawater collected from the Caribbean (St. Croix, American Virgin Islands). Standard deviations for the standards in each run varied with a long-term average of $\pm 0.3\%$.

In situ analyses

In situ analyses were performed on polished meteorite thin sections using the SIMS at UCLA. Samples included Cl-apatites from Zag (H3-6), Bjurböle (L/LL4), Tuxtuac (LL5), Saint-Séverin (LL6), and Bo Xian (LL3.9) as well as chondrule mesostasis and djerfisherite from Qingzhen. All thin sections were obtained from the IOM at UNM with the exception of Qingzhen chondrules, which were loaned to us by Alan Rubin of UCLA.

Chlorine-bearing phases were identified for SIMS analysis through examination of thin sections on the JEOL 5800LV scanning electron microscope (SEM) and JEOL 8200 electron microprobe at UNM. The identified Cl-bearing phases were then quantitatively analyzed on the electron microprobe. Typical electron microprobe conditions include an accelerating voltage of 15 kV, a 20nA beam current, and a 5µm beam diameter. More detailed descriptions of Cl-apatites and microprobe conditions of Cl-apatites analyses can be found in Jones and Dreeland (2010), Jones and Brearley (2010), and Jones et al. (2011a,b). Chondrule mesostases and djerfisherite in Qingzhen were quantitatively analyzed on the electron microprobe with an accelerating voltage of

15 kV, a beam current of 20 nA, and a 5 μm beam diameter to reduce volatilization of Na and Cl. Quantitative analyses of Qingzhen chondrule mesostases and djerfisherite can be found in Table 2 and 3, respectively. The average Cl content of the djerfisherite was 1.7 wt%.

Table 2: Mean mesostasis compositions for Qingzhen chondrules 3, 7, and 10. Chondrule 3 has two distinct regions of mesostasis: a Cl-rich and a Cl-poor region. Values are in wt %.

	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MgO	CaO	K ₂ O	Na ₂ O	SO ₃	Cl	Total
Ch 3												
Cl-rich	64.1	0.26	17.4	0.19	0.31	1.1	0.15	0.51	13.0	1.42	4.1	101.7
Cl-poor	68.4	0.01	19.1	0.01	0.11	0.77	0.28	0.20	11.3	0.20	0.02	100.5
Ch 7	58.7	0.28	22.3	0.08	0.21	2.8	3.8	0.26	10.3	1.1	1.4	100.8
Ch 10	55.9	0.45	21.9	0.14	0.53	6.8	0.28	0.33	13.2	1.5	1.8	102.5

Table 3: Analyses of djerfisherite grains in Qingzhen. Values are in wt %.

#	K ₂ O	Na ₂ O	FeO	CuO	NiO	ZnO	MnO	Cr ₂ O ₃	SO ₃	Cl	Total
dj4	8.5	0.65	49.6	3.0	1.3	0.19	0.64	0.00	32.7	1.7	98.3
dj6	8.6	0.66	49.0	2.5	1.3	0.16	0.81	0.00	33.3	1.8	98.1
dj7	8.6	0.65	49.5	2.7	1.4	0.06	0.64	0.04	33.0	1.7	98.2
dj8	8.3	0.77	50.0	2.8	1.3	0.00	0.64	0.00	32.6	1.7	98.2
dj10	8.2	0.72	48.6	2.8	1.2	0.20	0.26	0.04	32.0	1.7	95.8
dj11	8.2	0.72	48.9	2.8	1.2	0.14	0.51	0.02	32.1	1.7	96.2
dj12	8.5	0.64	47.8	2.9	1.2	0.00	0.00	0.00	31.9	1.7	94.7
dj13	8.3	0.78	49.1	3.0	1.3	0.08	0.26	0.07	32.3	1.7	96.9
dj14	8.4	0.63	50.1	3.0	1.2	0.00	0.00	0.00	32.4	1.7	97.4
dj15	8.5	0.70	49.5	2.4	1.3	0.00	1.32	0.00	33.6	1.8	99.0
dj16	8.3	0.79	50.4	2.8	1.3	0.00	1.53	0.00	32.8	1.7	99.7
dj17	8.7	0.61	50.2	3.0	1.2	0.00	0.00	0.02	32.5	1.7	97.9
dj22	8.3	0.70	48.1	2.8	1.4	0.30	0.94	0.00	32.2	1.6	96.4
dj23	8.6	0.62	50.4	3.1	1.4	0.00	0.00	0.00	33.1	1.7	99.0
dj24	8.5	0.71	49.2	3.1	1.4	0.21	2.21	0.00	33.2	1.7	100.3

SIMS analyses were performed on the Cameca ims-1270 at UCLA under the direction of Dr. Kevin McKeegan. ³⁷Cl and ³⁵Cl were analyzed as secondary ions in multi-collection mode in two faraday cups after being bombarded by a 10kV Cs⁺ primary beam with about a 2nA current. A spot size of about 20 μm was used as well as a 50 eV energy window. Care was taken to avoid cracks in grains that contained epoxy.

Standardization is relative to a synthetic apatite (6.8 wt% Cl), Durango apatite (0.37 wt% Cl), djerfisherite from Khibina massif (Kola peninsula, Russia) (1.2 wt% Cl), and a synthetic glass (1.3 wt% Cl). Count rates for ^{37}Cl on apatite standards average 1.5×10^7 counts/sec. Djerfisherite and synthetic glass standards averaged 2.1×10^7 counts/sec and 7.2×10^6 counts/sec, respectively. For the Cl-apatites from the O chondrites, standard deviations for the standards in each run on the SIMS were $\pm 0.6\%$. For chondrule mesostases and djerfisherite from Qingzhen, standard deviations of the standards were $\pm 1.1\%$. The $\delta^{37}\text{Cl}$ values of the standards were measured on the SIMS as well as on the IRMS. The value obtained from an IRMS analysis was used to correct the SIMS data.

To measure the $\delta^{37}\text{Cl}$ value of the glassy chondrule mesostasis in Qingzhen, we made a synthetic Cl-bearing glass with a composition that is similar to the average chondrule mesostases in Qingzhen. Oxide powders were mixed at UNM, and chlorine was added as NaCl. The powder was melted at a pressure of 8 GPa and temperature of 1000°C and quenched to a glass with the help of Jeremy Wykes and Craig Manning at UCLA. Electron microprobe analysis showed that we had a homogeneous glass with the following average composition: SiO_2 62.3 wt%, Al_2O_3 22.3 wt%, Na_2O 7.48 wt%, MgO 3.18 wt%, Cl 1.26 wt%, CaO 1.14 wt%, and K_2O 0.10 wt%. The $\delta^{37}\text{Cl}$ value of the synthetic glass, measured in continuous flow at UNM, is $0.89 \pm 0.54\%$. We also measured the Cl isotope composition of the NaCl that was added to the powder, and it had a $\delta^{37}\text{Cl}$ value of $-0.08 \pm 0.24\%$.

3: RESULTS

Chlorine concentration

To calculate the chlorine concentration of each sample, we used the area and voltage of the sample and standard. Knowing the Cl concentration of the seawater standard is 5.51 mg/L, which was measured using ion chromatography, we could calculate the Cl concentration of the sample in milligrams from the relationship between the sample and standard. The chlorine concentration in milligrams could then be converted to ppm by taking into account how much sample material was used. Chlorine concentrations were calculated for the SBC and WSC/leachate, and then these were combined to give a bulk sample concentration (Table 4). Bulk Cl concentrations were calculated by summing the Cl content (mg) from the SBC and WSC then dividing this value by the total sample weight. These values were converted to ppm by multiplying the calculated value by 10^6 . The error for the calculated chlorine concentrations of the samples is 19%.

In Fig. 2, we compare our data with literature values (Lodders and Fegley, 1998). As expected, our SBC data are generally less than literature values (bulk mean values), with the exception of CO and CK chondrites (Fig. 2a). However, our calculated bulk Cl concentrations are close to mean literature values (Fig. 2b). Figure 3 compares the bulk Cl content from previous studies of individual meteorites to the SBC content calculated in this study. SBC concentrations in this study range from 23 ppm (Itqiy) to 634 ppm (Orgueil), WSC concentrations range from 10 ppm (Ormans) to 567 ppm (Qingzhen), and bulk Cl concentrations range from 70 ppm (Sulagiri) to 991 ppm (Qingzhen) (Table 4). Figure 4 shows the relationship between bulk Cl concentration and petrologic type for all

chondrites analyzed. It is clear that in general there is a decrease in bulk Cl concentration with increase in petrologic type for all classes (Fig. 4). Enstatite chondrites show the strongest relationship, with concentrations of Cl decreasing from 991 in type 3 to 64 in type 7. Though O chondrites do not seem to show a correlation with decreasing Cl concentration and increasing petrologic type, if the y-axis is expanded and the O chondrites are split based on group, the LL chondrites exhibit this correlation from 196 ppm (Parnallee) to 83 ppm (Saint-Séverin) (Fig. 5).

Table 4: Summary of the $\delta^{37}\text{Cl}$ values and Cl concentrations for all chondrites analyzed. Data are divided into $\delta^{37}\text{Cl}$ values and Cl concentrations for SBC, WSC, and bulk. WSC and bulk concentration for Orgueil, Itqiy, Vigarano, and Bjurböle are in italics to signify that these values are questionable since they may contain terrestrial contamination in addition to WSC. All samples are falls except Itqiy and NWA6216.

	Group	Petrologic Type	SBC ppm	$\delta^{37}\text{Cl}_{\text{SBC}}$ (‰) vs SMOC	$\delta^{37}\text{Cl}_{\text{SBC}}$ 1 σ	WSC ppm	$\delta^{37}\text{Cl}_{\text{WSC}}$ (‰) vs SMOC	$\delta^{37}\text{Cl}_{\text{WSC}}$ 1 σ	$\Delta^{37}\text{Cl}$ (SBC-WSC)	Bulk Cl ppm	Bulk $\delta^{37}\text{Cl}$ (‰) vs SMOC
Carbonaceous Chondrites											
Orgueil	CI	1	634	-0.2	0.4	<i>342</i>	0.2	0.5	-0.4	<i>947</i>	-0.7
	CI	1	576	-2.0	0.5				-2.2		
Murray	CM	2	220	0.9	0.9	88	-1.8	0.3	2.6	308	0.1
NWA6216	CR	2	592	2.7	0.3	324	0.7	0.3	1.9	908	1.9
	CR	2	576	2.2	0.3				1.5		
Allende	CV	3	326	-0.3	0.4						
Vigarano	CV	3	138	-0.4	0.9	<i>126</i>	-0.4	0.3	0.0		-0.4
Kainsaz	CO	3.2	254	-0.5	0.5	57	-1.5	0.5	1.1	318	-0.8
	CO	3.2	267	-0.8	0.4				0.8		
Ornans	CO	3.4	290	-0.1	0.3	10				274	
	CO	3.4	212	0.2	0.1						
	CO	3.4	311	-0.2	0.1						
Karoonda	CK	4	322	-0.8	0.3	34				320	
	CK	4	251	-0.5	0.4						

Ordinary Chondrites											
Parnallee	LL	3.6	105	-4.0	0.1	66	-2.7	0.1	-1.4	196	-3.6
	LL	3.6	146	-4.3	0.2				-1.6		
	LL	3.6	138	-4.0	0.1				-1.4		
Dhajala	H	3.8	58	-0.6	0.1	13				89	
	H	3.8	94	-1.0	0.1						
Zag	H	3-6	126	-0.7	0.5	47	-1.8	0.5	1.0	173	-0.9
	H	3-6	90	-0.2	0.2	22				112	
Bjurböle	L/LL	4	96	-0.7	0.2	<i>45</i>	2.4	0.1	-3.2	<i>113</i>	2.5
	L/LL	4	47	-0.6	0.1				-3.1		
Tuxtuac	LL	5	51	1.0	0.1	49	0.1	0.3	0.9	122	1.0
	LL	5	98	0.6	0.3				0.5		
Sulagiri	LL	6	68	-0.5	0.3	21				70	
	LL	6	30	-0.2	0.3						
Saint-Séverin	LL	6	133	-1.7	0.4						
	LL	6	70	-1.0	0.2	14				83	
	LL	6	69	-0.6	0.1						

Table 4: continued

	Group	Petrologic Type	SBC ppm	$\delta^{37}\text{Cl}_{\text{SBC}}$ (‰) vs SMOC	$\delta^{37}\text{Cl}_{\text{SBC}}$ 1 σ	WSC ppm	$\delta^{37}\text{Cl}_{\text{WSC}}$ (‰) vs SMOC	$\delta^{37}\text{Cl}_{\text{WSC}}$ 1 σ	$\Delta^{37}\text{Cl}$ (SBC-WSC)	Bulk Cl ppm	Bulk $\delta^{37}\text{Cl}$ (‰) vs SMOC
Enstatite Chondrites											
Qingzhen	EH	3	510	0.0	0.4	567	0.9	0.4	-0.9	991	1.5
	EH	3	349	0.2	0.4				-0.7		
Abee	EH	4	441	0.3	0.3	336	-0.2	0.3	0.5	740	0.0
	EH	4	365	0.1	0.1				0.3		
Itqiy	EH	7	32	-1.7	0.3	36	0.6	0.3	-2.3	64	
	EH	7	23	-2.1	0.3				-2.7		
Eagle	EL	6	192	0.1	0.1	30				211	
	EL	6	169	0.4	0.3						
Yilmia	EL	6	219	0.9	0.1	55	0.5	0.3	0.5	294	0.8
	EL	6	261	0.8	0.1				0.3		

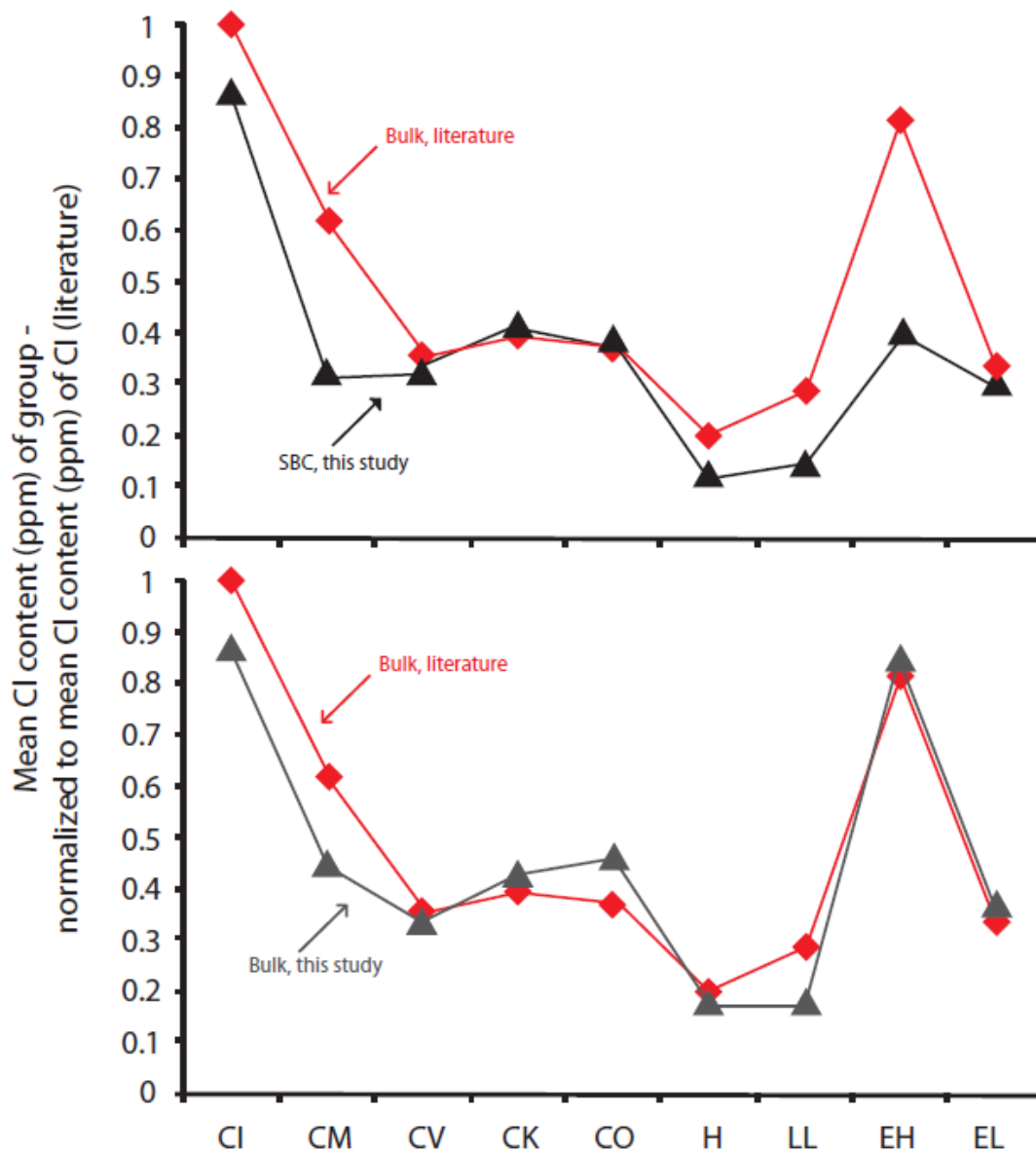


Figure 2: Comparison of Cl concentration for SBC and bulk chondrite data (this study) with literature values. Diamond symbols and red lines represent literature data (Lodders and Fegley, 1998). Mean Cl content (ppm) of each chondrite group is normalized to mean literature value for CI chondrites (700 ppm). Mean values from this study represent all analyses for the group including duplicates or triplicates. a) Mean SBC Cl content (ppm) of each chondrite group. Triangles and black line represent SBC concentrations from this study. b) Mean bulk Cl content (ppm) of each chondrite group. Grey line represents bulk concentrations from this study. SBC concentrations were used in the means instead of bulk Cl content for Itqiy and Orgueil since the prewash to remove terrestrial Cl⁻ was not done for these two samples.

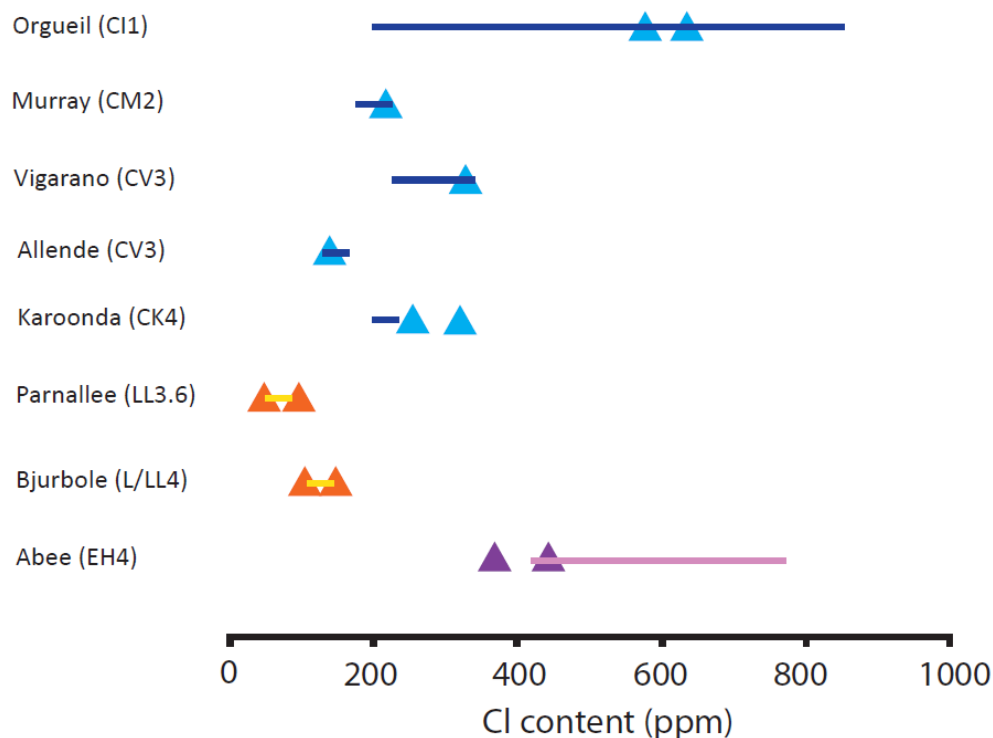


Figure 3: Comparison of the bulk Cl content (ppm) determined by previous authors (lines) with SBC Cl content calculated in this study (triangles) with same color scheme as in Fig. 1. Ranges include values from Greenland et al. (1965), Reed et al. (1966), Goles et al. (1967), Dreibus et al. (1979), Tartar (1981), Magenheim et al. (1995), Garrison et al. (2000), Bonifacie et al. (2007), Sharp et al. (2007), and Nakamura et al. (2011).

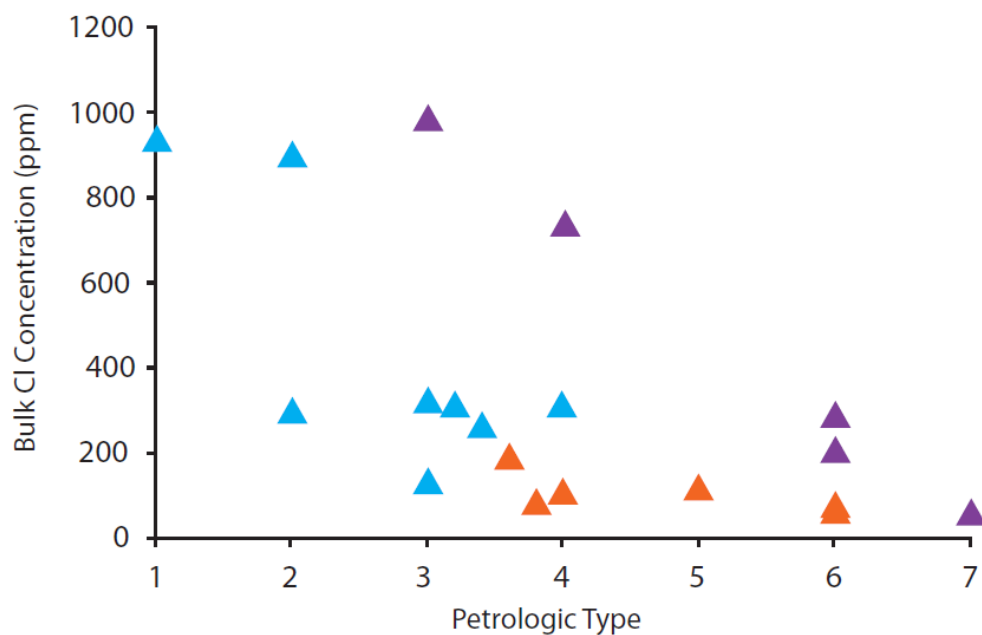


Figure 4: Bulk Cl concentration (ppm) versus petrologic type for all chondrites analyzed. Carbonaceous chondrites are in blue, ordinary chondrites in orange, and enstatite chondrites in purple.

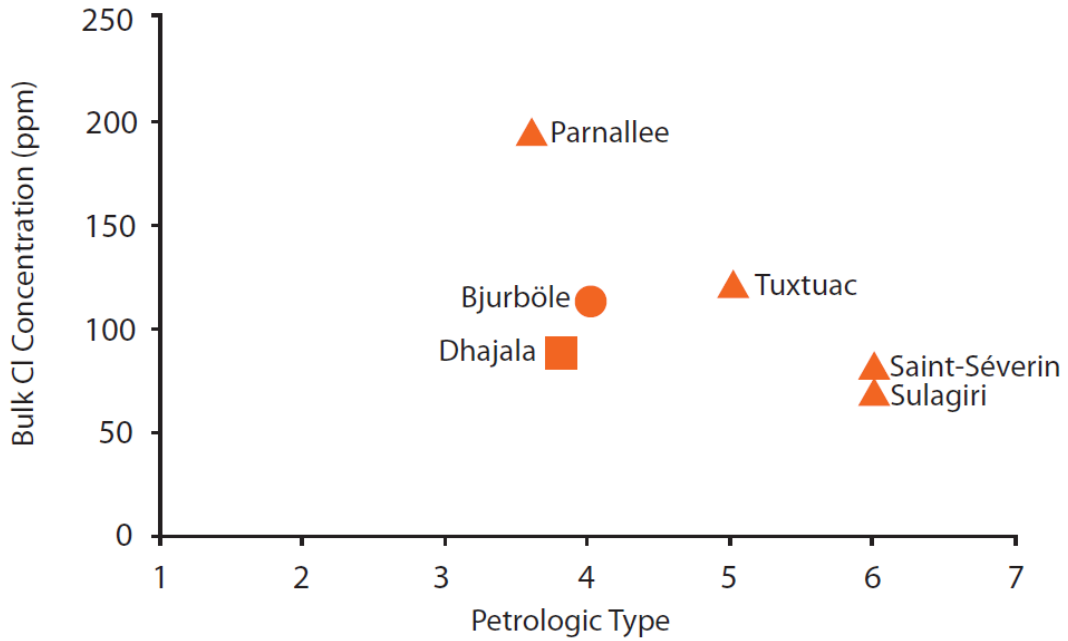


Figure 5: Bulk Cl concentration (ppm) versus petrologic type for ordinary chondrites. LL chondrites are triangles. H chondrite is a square. L/LL chondrite is a circle.

$\delta^{37}\text{Cl}$ values of Structurally Bound and Water Soluble Chloride

$\delta^{37}\text{Cl}_{\text{SBC}}$, $\delta^{37}\text{Cl}_{\text{WSC}}$, and $\delta^{37}\text{Cl}_{\text{Bulk}}$ values from chondrites analyzed are summarized in Table 4. Calculated bulk $\delta^{37}\text{Cl}$ values are also included in Table 4. Bulk $\delta^{37}\text{Cl}$ values for some samples were calculated using the formula $(\delta^{37}\text{Cl}_{\text{SBC}})(X_{\text{SBC}}) + (\delta^{37}\text{Cl}_{\text{WSC}})(X_{\text{WSC}})$ where X_{SBC} and X_{WSC} are mole fractions of SBC and WSC, respectively. The mole fractions of SBC and WSC were calculated from the sample peak size. For the WSC that had an area less than 200 millivolts • sec, the measured $\delta^{37}\text{Cl}_{\text{WSC}}$ values tended to be unreasonably negative. These values were considered unreliable so a bulk $\delta^{37}\text{Cl}$ was not calculated with the addition of the WSC contribution. However, the mole fractions of the WSC were so small that they had only a minimal effect of about 0.1‰ on the calculated bulk $\delta^{37}\text{Cl}$ value.

Figure 6 displays the $\delta^{37}\text{Cl}_{\text{SBC}}$ and $\delta^{37}\text{Cl}_{\text{WSC}}$ values for all chondrites analyzed (average = -0.5‰ , $n=40$). $\delta^{37}\text{Cl}$ values range from -4.3‰ (Parnallee) to 2.7‰ (NWA6216). Carbonaceous chondrite $\delta^{37}\text{Cl}$ values range from -2.0‰ (Orgueil) to 2.7‰ (NWA6216) and average -0.13‰ ($n=19$). Ordinary chondrite $\delta^{37}\text{Cl}$ values range from -4.25‰ (Parnallee) to 2.4‰ (Bjurböle leachate) and average -1.0‰ ($n=20$). Enstatite chondrite $\delta^{37}\text{Cl}$ values range from -2.1‰ (Itqiy) to 0.9‰ (Yilmia) and average 0.05‰ ($n=14$). Water soluble chloride may have either lower or higher $\delta^{37}\text{Cl}$ values than the corresponding SBC (Fig. 6). However, there is a question about the reliability of the data for WSC from Orgueil, Itqiy, Bjurböle, and Vigarano. For the Orgueil and Itqiy samples, we did not do a first rinse because Orgueil disintegrated when placed in deionized water and Itqiy was accidentally crushed before rinsing. For these two samples the leachate could be representative of the WSC in the sample and/or terrestrial contamination. In the case of Bjurböle, the meteorite fell into a frozen lake and this may have affected the $\delta^{37}\text{Cl}$ value of the WSC. The Vigarano fall consisted of two stones, one that was collected immediately after the fall and one that was collected a month later. The piece of Vigarano that was analyzed in this study is from the second stone that has experienced terrestrial weathering (Abreu and Brearley, 2005).

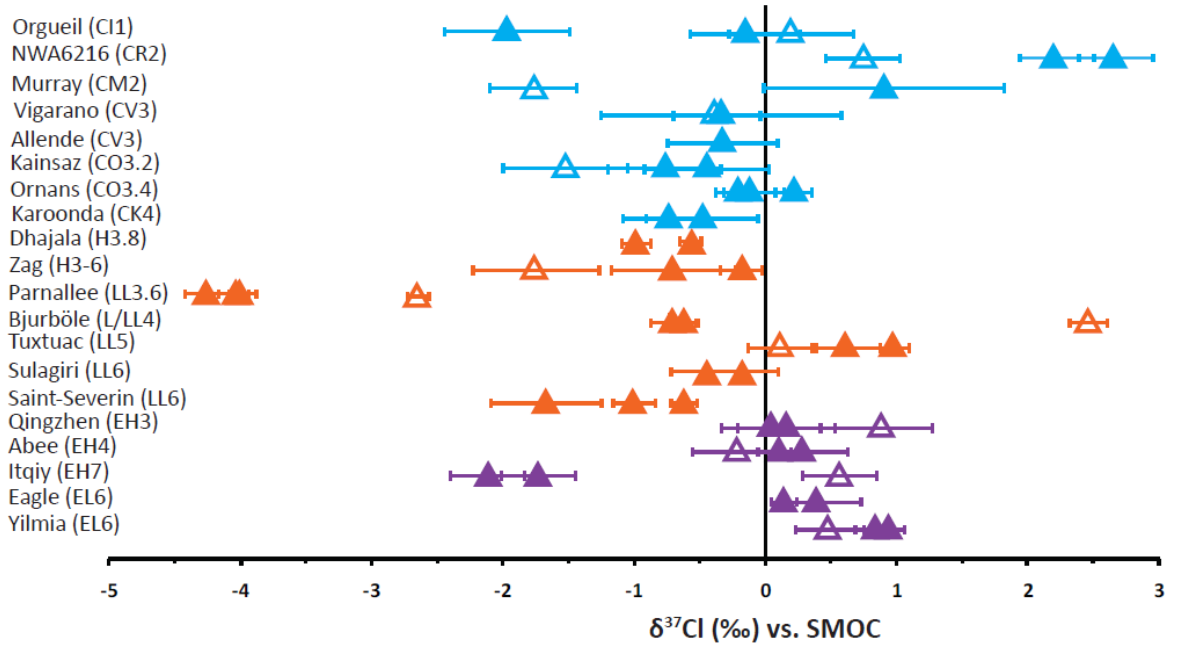


Figure 6: $\delta^{37}\text{Cl}$ values of chondrites analyzed in this study. Each line represents a separate chondrite. Samples are divided based on chondrite class with carbonaceous chondrites in blue, ordinary chondrites in orange, and enstatite chondrites in purple. Error bars represent one sigma standard deviation of the standards that were analyzed on the same day for each particular sample. Open symbols represent WSC while closed symbols represent SBC.

In Fig. 7, bulk $\delta^{37}\text{Cl}$ values are shown for Murray, NWA6216, Vigarano, Kainsaz, Zag, Parnallee, Bjurböle, Tuxtuac, Abee, Qingzhen, and Yilmia. These eleven chondrites are the only samples for which we were able to calculate bulk $\delta^{37}\text{Cl}$ values. Bulk $\delta^{37}\text{Cl}$ values range from -3.6 (Parnallee) to 2.5‰ (Bjurböle).

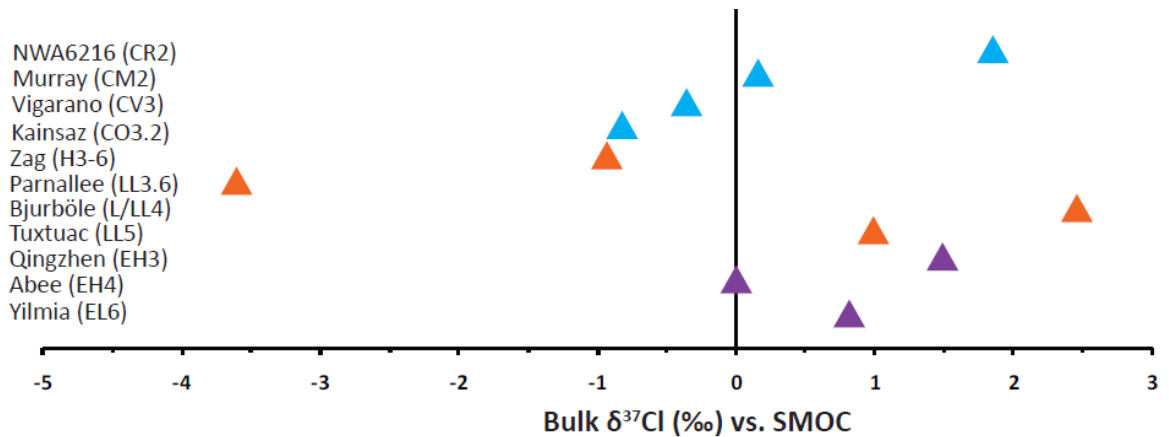


Figure 7: Bulk $\delta^{37}\text{Cl}$ values of chondrites for which both WSC and SBC were measured. Bulk $\delta^{37}\text{Cl}$ values were calculated using the formula $(\delta^{37}\text{Cl}_{\text{SBC}})(X_{\text{SBC}}) + (\delta^{37}\text{Cl}_{\text{WSC}})(X_{\text{WSC}})$. Color scheme as in Fig. 1.

Figure 8 shows the relationship between $\delta^{37}\text{Cl}_{\text{SBC}}$ and SBC Cl concentration for individual chondrites. O chondrites have the lowest and most restricted range of Cl concentration, but the largest range in $\delta^{37}\text{Cl}$ values. C and E chondrites have wide ranges of Cl concentration and more restricted ranges of $\delta^{37}\text{Cl}$ values. There is no clear relationship between Cl concentration and $\delta^{37}\text{Cl}$ for any of the classes.

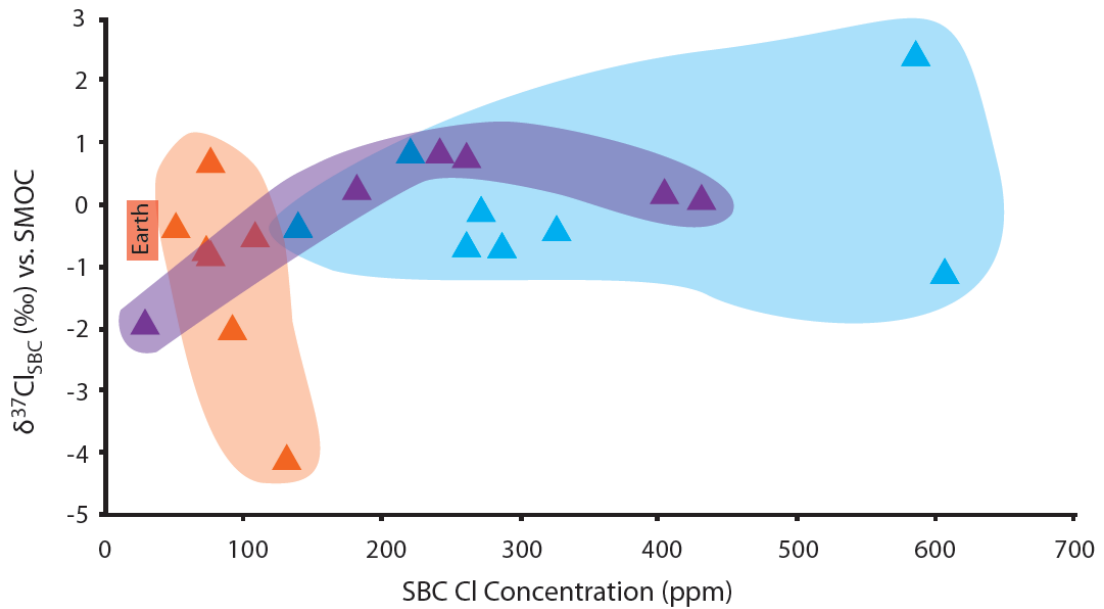


Figure 8: Average $\delta^{37}\text{Cl}_{\text{SBC}}$ values plotted against average SBC Cl concentration. C, O, and E chondrite fields are outlined with same color scheme as in Fig. 1. $\delta^{37}\text{Cl}$ value and Cl concentration range for the bulk Earth are plotted in the rectangle (Sharp et al., 2007).

Figure 9 compares the bulk $\delta^{37}\text{Cl}$ and bulk Cl concentration for the eleven above-mentioned samples. We do not see much change in the overall locations of classes when comparing Fig. 7 to Fig. 8 except now the E chondrite field no longer overlaps the O chondrite field.

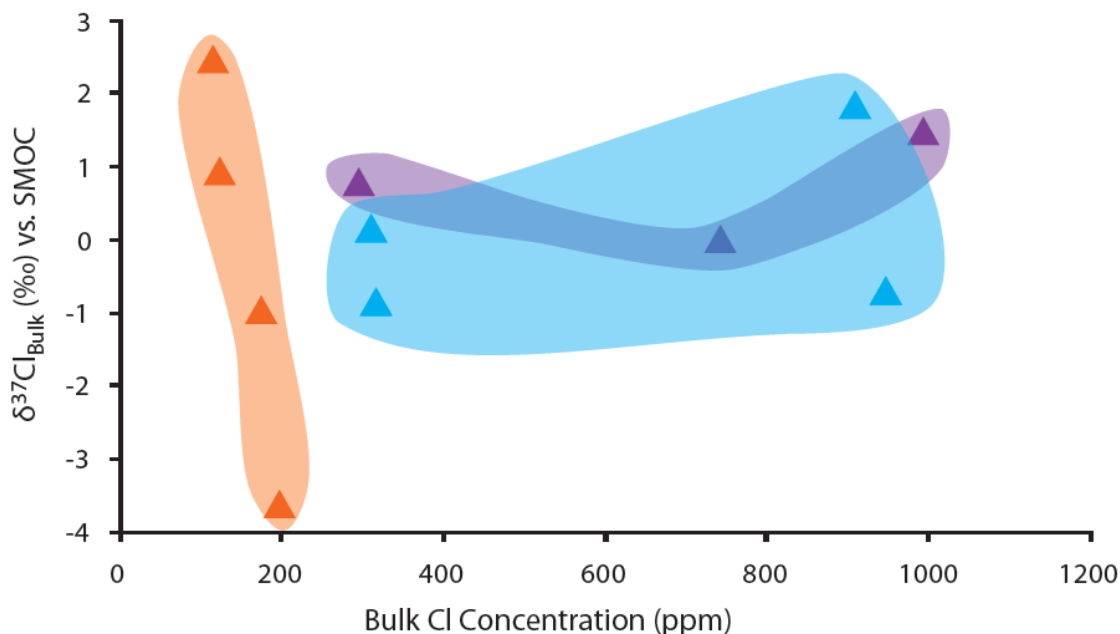


Figure 9: $\delta^{37}\text{Cl}_{\text{Bulk}}$ values plotted against bulk Cl concentration. C, O, and E chondrite fields are outlined with same color scheme as in Fig. 1

SIMS analyses of Cl-bearing phases

Chlorine-bearing phases, identified by SEM and electron microprobe, must have grain diameters greater than the Cs^+ beam ($\sim 10\text{-}15\mu\text{m}$) for measurement by SIMS. Zag, a chondrite from the H group of the O chondrites, is a regolith breccia with light and dark clasts that range in petrologic type from 3 to 6 (Rubin et al., 2002). Our thin section had both light and dark clasts of petrologic type 6 and 4, respectively (Jones et al., 2011a). We analyzed Cl-apatites from both types of clasts. Of the Cl-apatites analyzed in Tuxtuac (LL5), two were located inside a chondrule and one was in the matrix. Cl-apatites from Bo Xian (LL3.9) and Bjurböle (L/LL4) were also in the matrix. Cl-apatites in Saint-Séverin are associated with merrillite grains and are located near shock features such as chromite-plagioclase assemblages (Jones and Dreeland, 2010). Examples of these apatite grains are shown in Fig. 10. Chlorine-bearing chondrule mesostasis and djerfisherite were analyzed in thin sections of Qingzhen. We analyzed glassy Cl-rich mesostasis from three

chondrules, two porphyritic olivine pyroxene chondrules and one radial pyroxene chondrule. Djerfisherite grains are located throughout the thin section, outside of chondrules. Most grains have begun to react and break down to secondary troilite which is called the Qingzhen reaction (El Goresy et al., 1988). Examples of chondrule mesostasis and djerfisherite are found in Fig. 10.

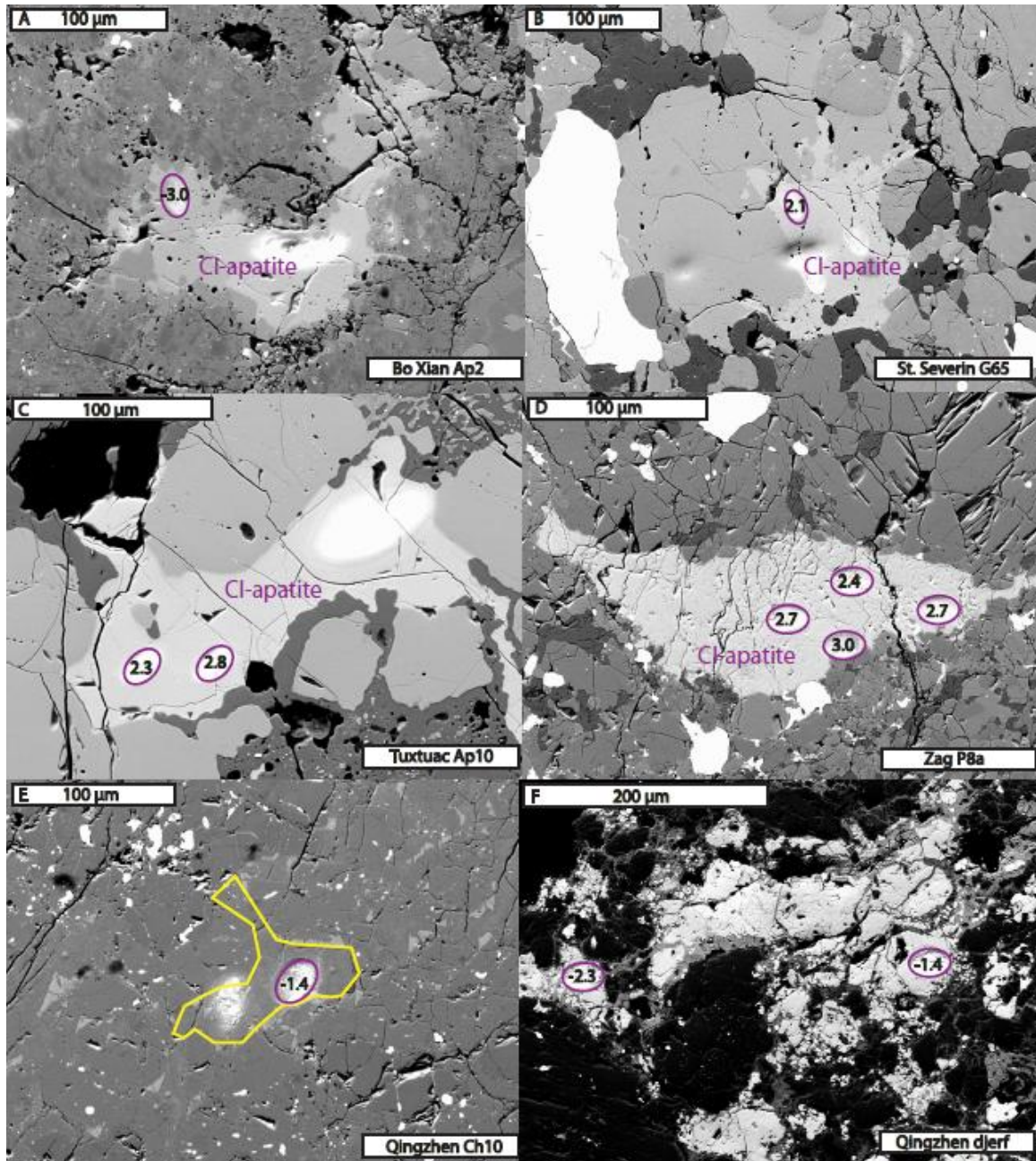


Figure 10: Backscattered electron images of individual grains analyzed by SIMS. SIMS spots outlined in purple with $\delta^{37}\text{Cl}$ values (‰) of the spots in the outline. Cl-apatites are from the following samples: a) Bo Xian, b) Saint-Séverin, c) Tuxtuac, and d) Zag. Larger spots on the apatite grains are from previous SIMS analyses for OH^- (Jones et al., 2011a). Analyses from Qingzhen include e) chondrule 10 mesostasis (outlined in yellow) and f) djerfisherite.

The $\delta^{37}\text{Cl}$ values for *in situ* measurements are given in Table 5 and shown in Fig.

11. Chlorine contents in Table 5 were determined by electron microprobe analysis and can be found in more detail in Tables 2 and 3. For the O chondrites, three of the samples

showed a wide range of $\delta^{37}\text{Cl}$ values. Fourteen analyses on four apatite grains in Zag range in $\delta^{37}\text{Cl}$ values from -0.6 to 2.9‰. Five analyses on three apatite grains in Tuxtuac range from 1.6 to 4.6‰. Three analyses on two Saint-Séverin apatite grains range from 0.9 to 2.9‰. In contrast, analyses on Bo Xian and Bjurböle apatites showed a more limited range, -3.0 to -2.9‰ ($n=2$) and -1.5 to -1.1‰ ($n=2$), respectively. In Qingzhen (EH3), a total of 10 points were analyzed on the chondrule mesostasis in three separate chondrules and four points were analyzed on four separate grains of djerfisherite. Chondrule mesostasis $\delta^{37}\text{Cl}$ values ranged from -2.5 to 1.3‰ while djerfisherite values ranged from -2.3 to -0.5‰.

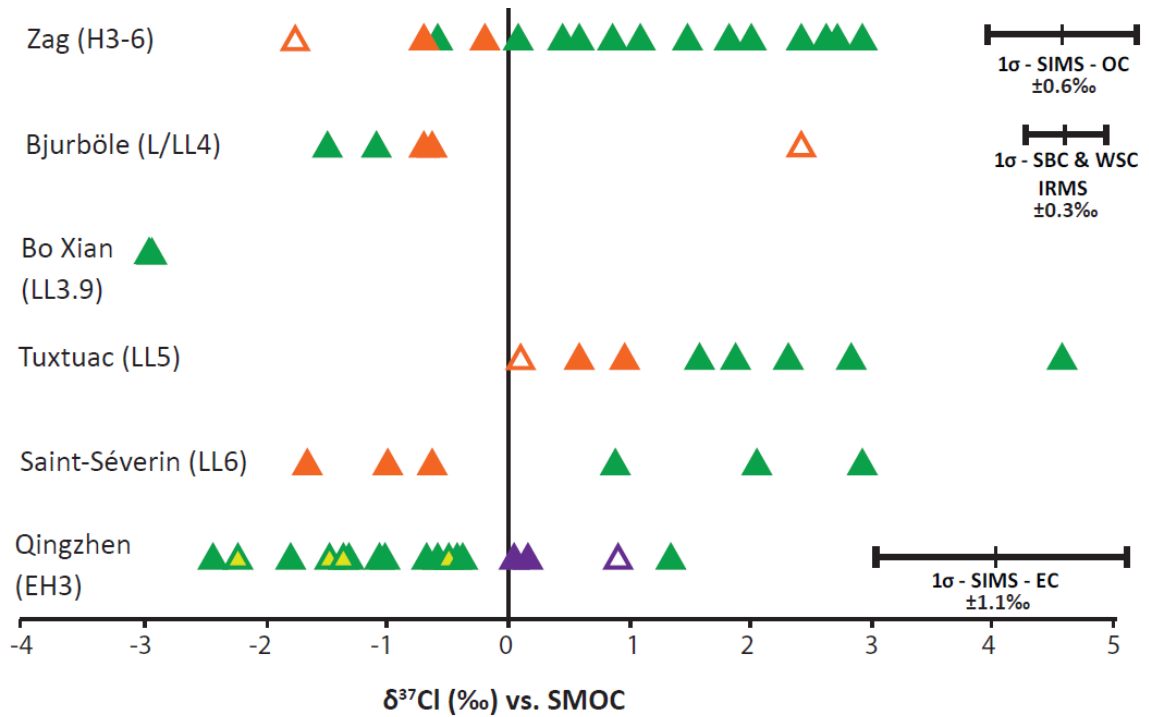


Figure 11: $\delta^{37}\text{Cl}$ values obtained from SIMS analyses (green) compared with $\delta^{37}\text{Cl}_{\text{SBC}}$ values (filled orange and purple) and $\delta^{37}\text{Cl}_{\text{WSC}}$ values (unfilled orange and purple). For Qingzhen (EH3), djerfisherite grains (light green with green border) are differentiated from chondrule mesostasis (green).

Table 5: $\delta^{37}\text{Cl}$ values measured by SIMS for Cl-apatites from OC and chondrule mesostases and djerfisherite from Qingzhen (EH3). 1σ standard deviations are $\pm 0.6\text{‰}$ for OC and $\pm 1.1\text{‰}$ for Qingzhen.

Chondrite	Grain	Cl content (wt %)	$\delta^{37}\text{Cl}$ (‰)
Ordinary Chondrites - Cl-apatites			
Zag (H3-6)	M2D	5.7	1.1
<i>Thin Section UNM1136</i>	M2D		1.8
	M2D		0.1
	M2D		2.0
	M2D		0.4
	M2D		-0.2
	M2D		-0.6
	P8a	5.4	2.7
	P8a		2.4
	P8a		2.6
	P8a		2.9
	P8b	5.8	1.5
	P13	6.2	0.6
	P13		0.9
Bo Xian (LL3.9)	Ap2	4.4	-3.0
<i>Thin Section UNM265</i>	Ap2		-2.9
Tuxtuac (LL5)	Ap10-1	4.6	1.6
<i>Thin Section UNM627</i>	Ap10-1		1.9
	Ap10-2		2.8
	Ap10-2		2.3
	Ap5		4.6
Saint-Severin (LL6)	G43	5.0	2.9
<i>Thin Section UNM693</i>	G65	4.9	0.9
	G65		2.1
Enstatite Chondrite - Qingzhen (EH3)			
Chondrule 3	mesostasis	4.1	-1
<i>Thin section 611</i>	mesostasis	4.1	1.3
	mesostasis	4.1	-0.7
	mesostasis	4.1	-0.4
	mesostasis	4.1	-0.4
Chondrule 7	mesostasis	1.4	-0.4
<i>Thin section 612</i>	mesostasis	1.4	-2.5
	mesostasis	1.4	-0.6
	mesostasis	1.4	-0.6
Chondrule 10	mesostasis	1.8	-1.8
<i>Thin section 612</i>	mesostasis	1.8	-3.3
	mesostasis	1.8	-1.4
	mesostasis	1.8	-1.1
	mesostasis	1.8	-1.1
Djerfisherite	dj10	1.7	-1.4
<i>Thin Section UNM636</i>	dj12	1.7	-2.3
	dj17	1.7	-1.5
	dj16	1.7	-0.5
	dj16	1.7	-0.5

4: DISCUSSION

Type 3 chondrites - Homogeneous or heterogeneous nebula?

We analyzed type 3 chondrites from the O, C, and E classes in order to determine whether the nebula had a homogeneous chlorine isotope composition or if multiple isotope reservoirs existed. For oxygen and, to a lesser extent, nitrogen, individual chondrite groups have markedly different isotopic signatures (e.g. Kung and Clayton, 1978; Clayton, 1993). Oxygen isotope compositions of chondrites are even used to distinguish among the chondrite groups in the C, O, and E classes (Clayton, 1993). We were interested in determining if chlorine isotopes behave similarly to oxygen and nitrogen and vary among the chondrite groups and/or classes. To test this, we measured the $\delta^{37}\text{Cl}$ value of the least equilibrated and least altered chondrites, petrologic type 3 (Van Schmus and Wood, 1967). Type 3 chondrites should preserve an unaltered nebular $\delta^{37}\text{Cl}$ signature. Type 3 chondrites in our study include Qingzhen (EH3), Kainsaz (CO3.2), Ornans (CO3.4), Vigarano (CV3), Allende (CV3), Dhajala (H3.8), and Parnallee (LL3.6). All of these have similar $\delta^{37}\text{Cl}$ values with the exception of Parnallee, which will be discussed later. A student's t-test of the means was used to compare the means of the type 3 chondrites from each class (excluding Parnallee) in order to determine if the $\delta^{37}\text{Cl}$ values of the classes were unique. Using the $\delta^{37}\text{Cl}$ values of each sample (including duplicates), we ran a two-tailed test with a 10% significance level and found that the means of the type 3 chondrites from each class are not statistically different. We can thus calculate an average type 3 $\delta^{37}\text{Cl}$ value, excluding Parnallee and Allende, which has a $\delta^{37}\text{Cl}$ value of $-0.3 \pm 0.4\text{‰}$. We exclude Allende because it is an oxidized CV chondrite, which may have experienced aqueous alteration as well as

heating on its chondrite parent body (Brearley, 2005). However, including Allende does not change the type 3 mean while the inclusion of Parnallee causes the average to become more negative at a $\delta^{37}\text{Cl}$ value of -1.1‰. Because the means of the unequilibrated chondrites from each class are statistically the same, we argue that the inner solar nebula had a homogeneous chlorine isotope composition of $-0.3 \pm 0.4\text{‰}$. This value is similar to the $\delta^{37}\text{Cl}$ values for the range of the bulk Earth (-1.0 to 0.4‰) (Sharp et al., 2007), the lowest measured value for the Moon (-0.7‰) (Sharp et al., 2010b), and the average of several martian meteorite samples (-0.4‰) (Sharp et al., 2011a), which is consistent with a single homogeneous chlorine isotope reservoir in the inner solar nebula and supports a near zero bulk $\delta^{37}\text{Cl}$ value for the Earth.

Parent Body Processes

During the first tens of millions of years following accretion, temperatures on the chondrite parent bodies increased as a result of the decay of short-lived radioisotopes such as ^{26}Al (e.g. MacPherson et al., 1995). This temperature increase resulted in the melting of ice and mobilized fluids that aqueously altered pristine chondritic material. Further temperature increases resulted in metamorphism of pristine material to various degrees (Brearley and Jones, 1998). Although long considered a dry process, evidence has been found for the presence of water during metamorphism (Brearley, 2006).

The degree to which a chondrite has been altered, by either water or heat, is described by the petrologic type classification scheme developed by Van Schmus and Wood (1967). Type 3 chondrites are considered the most unaltered material, with highly unequilibrated mineral compositions. Increasing degrees of aqueous alteration are defined

by petrologic types 2 and 1. Type 1 chondrites are the most aqueously altered.

Carbonaceous chondrites are the only chondrites that have been classified as types 1 and 2. The degree of metamorphism increases from type 3 to type 6 (Van Schmus and Wood, 1967). Type 7 is the highest degree of metamorphism, though not commonly used, and may indicate that the sample has seen some partial melting. For CO, CV, and O chondrites, type 3s are further subdivided into 10 subtypes, 3.0 to 3.9, to designate various degrees of metamorphism (Keck and Sears, 1987; Sears et al., 1991).

Possible Fractionations in the Solar Nebula and on Parent Bodies

In order to understand the processes that could fractionate the Cl isotopes and cause variations among the altered chondrites, we constructed a schematic diagram illustrating possible fractionation processes (Fig. 12). Figure 13 shows average $\delta^{37}\text{Cl}$ values of analyzed chondrites plotted in the same orientation as Fig. 13 in order to facilitate comparison between predicted and observed $\delta^{37}\text{Cl}$ values.

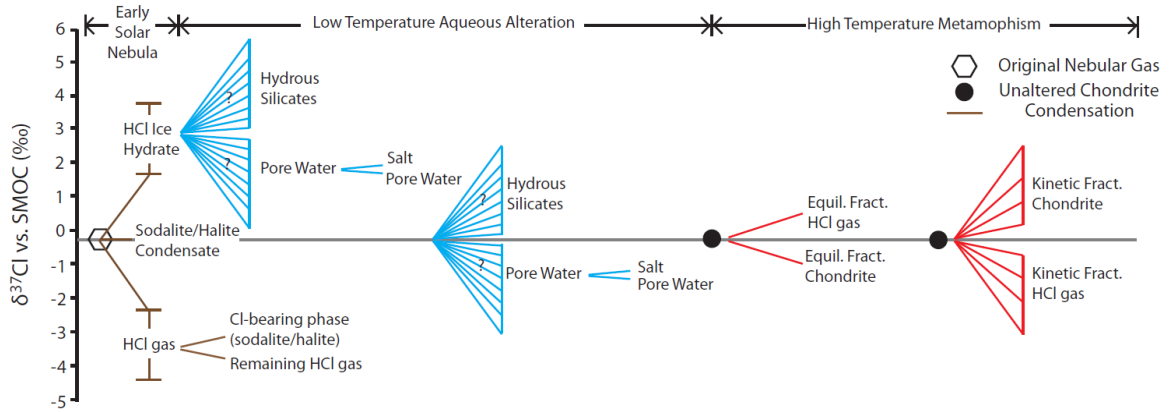


Figure 12: Schematic diagram for visualizing possible fractionations in chondrite samples assuming that the original nebular gas had a $\delta^{37}\text{Cl}$ value of -0.3‰ . Plotted along the x-axis are possible fractionation mechanisms. The horizontal line at -0.3‰ indicates the $\delta^{37}\text{Cl}$ value of type 3 unaltered chondrites. Fractionation ranges are given for processes where we do not know the magnitude of fractionation. Fractionation between HCl gas and HCl hydrate is $4\text{--}6\text{‰}$ (Schauble and Sharp, 2011). Fractionation between HCl gas and sodalite is 0.8‰ (Schauble and Sharp, 2011). Fractionation between halite and aqueous solution is 0.26‰ (Eggenkamp et al., 2001). Fractionation between hydrous silicates and pore water and salts and pore water could occur during aqueous alteration (Ransom et al., 1995). Fractionation between HCl gas and aqueous HCl of around 1.5‰ was determined experimentally by Sharp et al. (2010a). Equilibrium and kinetic fractionation between HCl gas and Cl-bearing phases in a chondrite could occur during metamorphism.

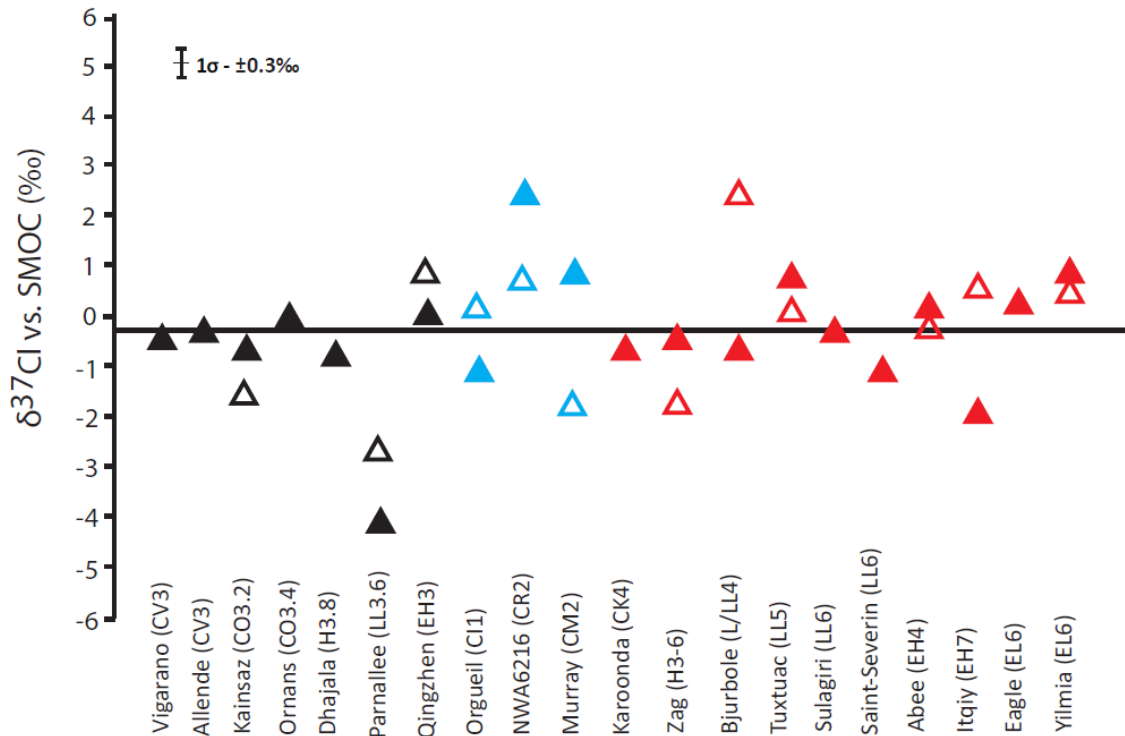


Figure 13: Mean $\delta^{37}\text{Cl}_{\text{SBC}}$ and $\delta^{37}\text{Cl}_{\text{WSC}}$ values of chondrites plotted in the same orientation as the fractionation schematic in Fig. 12. Petrologic type 3 chondrites are in black, type 4-6 are in red, and type 1-2 are in blue.

We consider that there are three possible processes for incorporating chlorine into chondritic materials: 1) Partial condensation of chlorine from the nebular gas as a salt (NaCl or KCl) or in sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$), 2) Partial condensation of HCl hydrate ($\text{HCl} \cdot 3\text{H}_2\text{O}$) from the nebular gas and subsequent melting of the hydrate on a parent body, or 3) Condensation of HCl gas that remains after partial $\text{HCl} \cdot 3\text{H}_2\text{O}$ condensation into chondrule melts during chondrule formation events. Isotopic fractionation during these processes will only occur if the process is partially completed. For example, if all the HCl gas in the nebula condensed as sodalite, no fractionation would occur. Sodalite that has partially condensed from nebular HCl gas will have a $\delta^{37}\text{Cl}$ value about 0.8‰ less than the coexisting HCl gas (Schauble and Sharp, 2011). Halite will have a similar fractionation to sodalite. The largest fractionation occurs during condensation of $\text{HCl} \cdot 3\text{H}_2\text{O}$ from HCl gas. Over the expected temperature range of $\text{HCl} \cdot 3\text{H}_2\text{O}$ condensation, 140 to 160K, $\text{HCl} \cdot 3\text{H}_2\text{O}$ will have $\delta^{37}\text{Cl}$ values 4 to 6‰ greater than the coexisting HCl gas (Schauble and Sharp, 2011). If processes 2 and 3 were significant in the solar nebula, we would expect the $\delta^{37}\text{Cl}$ values of chondrites to range from 2 to 4‰ or -2 to -4‰, depending if process 2 or 3 occurred respectively. However, with the exception of Parnallee, we do not observe such large fractionations (Fig. 13). Therefore, we conclude that processes 2 and 3 do not play significant roles as the source of chlorine and in determining $\delta^{37}\text{Cl}$ values of chondrites. It appears that the dominant process was process 1, partial condensation of chlorine as halite or sodalite.

In order to understand the fractionations that may have occurred during secondary processes, we can compare studies of terrestrial samples and experimental data that resemble the processes that may have taken place on chondrite parent bodies. During

aqueous alteration, fluids interacted with chondritic material and produced hydrous phases and salts (Brearley, 2006). The possible fractionations during these processes will be discussed first before explaining the layout of processes in Fig. 12. Ransom et al. (1995) measured the $\delta^{37}\text{Cl}$ values of subduction-zone pore waters and compared them to previously measured values for hydrous phases, including amphiboles and smectites. These authors found that the subduction-zone pore waters ranged in $\delta^{37}\text{Cl}$ values from 0.31 to -7.71‰ (Ransom et al., 1995). Comparing these values to those of smectite and amphiboles measured by Magenheimer et al. (1994), Ransom et al. (1995) concluded that the formation of hydrous phases incorporates ^{37}Cl preferentially and lowers the $\delta^{37}\text{Cl}$ values of the pore water (Ransom et al., 1995). However, there is a problem with this interpretation because the $\delta^{37}\text{Cl}$ values of the pore waters and hydrous phases were measured by TIMS, so the magnitude of the fractionation is probably not correct and the corresponding high $\delta^{37}\text{Cl}$ values of hydrous phases have not been found to date. In Fig. 12 fractionation between hydrous phases and pore waters are shown covering a wide range of $\delta^{37}\text{Cl}$ values, to indicate this uncertainty. In addition to fractionation between pore water and hydrous phases, fractionation may also occur during the precipitation of salts from a fluid. Eggenkamp et al. (1995) experimentally determined the fractionation between halite and aqueous solution. Halite will also preferentially incorporate ^{37}Cl and will have $\delta^{37}\text{Cl}$ values around 0.26‰ greater than the solution. These processes are illustrated in Fig. 12 in blue for aqueous alteration. In the presence of a fluid on the chondrite parent body, hydrous phases and salts may be produced, and we would expect to observe the following trends: hydrated silicates will have a greater $\delta^{37}\text{Cl}$ value than a salt that precipitates from the same fluid. In the figure, there are two examples of how

aqueous alteration could produce very different $\delta^{37}\text{Cl}$ values. These include the alteration of pristine, presumably anhydrous, chondritic material by melted HCl hydrate, which would result in high positive $\delta^{37}\text{Cl}$ values, or by a fluid that has a similar $\delta^{37}\text{Cl}$ value to the starting material, which would result in small positive or negative $\delta^{37}\text{Cl}$ values.

During metamorphism, chondritic material experienced temperatures ranging from 600 to 950°C. If Cl is present in phases that are unstable at these temperatures, it may be volatilized and there may be fractionation of the Cl isotopes. One possible fractionation mechanism occurs as a result of the higher translational velocity of the isotopologues of ^{35}Cl , such as H^{35}Cl , relative to ^{37}Cl isotopologues, which is referred to as kinetic fractionation, or Rayleigh fractionation (Sharp, 2007). This process will cause the $\delta^{37}\text{Cl}$ value of a solid (or liquid) Cl-bearing phase to shift to higher (more positive) $\delta^{37}\text{Cl}$ values as volatilization proceeds, as long as the system is open and volatilized gas is allowed to escape. In Fig. 12, kinetic fractionation is shown covering a range of $\delta^{37}\text{Cl}$ values to indicate that continued loss of H^{35}Cl , or other species, to the gas phase will drive the $\delta^{37}\text{Cl}$ values of the Cl-bearing phases to higher values. Another possible fractionation that might occur during volatilization is equilibrium fractionation between HCl gas and Cl-bearing phases. During this process, the covalent bond between H and Cl will preferentially incorporate ^{37}Cl leaving the Cl-bearing phases in the chondrite with a 1.5‰ lower $\delta^{37}\text{Cl}$ value than before metamorphism began (Schauble et al., 2003; Sharp et al., 2010a). Therefore, as a result of metamorphism, the Cl-bearing phases in a chondrite may show a decrease or increase in $\delta^{37}\text{Cl}$ value. As temperatures increase, the extent of fractionation between Cl-bearing phases and volatilized gas will most likely decrease as

in other isotopic systems (Sharp, 2007; Schauble and Sharp, 2011). These fractionations are illustrated in Fig. 12 and are colored red for metamorphism.

Aqueously altered samples – Types 1-2

Aqueous alteration effects have been observed mainly in C chondrites and also in some O chondrites (e.g. Grossman et al., 2000). The proposed sources of water for alteration include water vapor present in the solar nebula and water ice that has accreted onto the chondrite parent body (Brearley, 2006). An ice hydrate containing HCl has also been proposed to form between 140 to 160 K (Zolotov and Mironenko, 2007) and could be a source of chlorinated water for alteration. This ice would then be melted and mobilized during a low temperature event, less than 300°C, to alter chondritic material (e.g. Brearley and Jones, 1998; Brearley, 2006). If this is the case, the chlorinated ice hydrate will strongly incorporate ^{37}Cl , and this should be manifest in the aqueously altered material. The fact that this is not seen suggests that partial conversion of HCl (g) to $\text{HCl}\cdot 3\text{H}_2\text{O}$ was not an important process for the formation of hydrous fluids/ice or that accretion of chondrites occurred before $\text{HCl}\cdot 3\text{H}_2\text{O}$ condensed and hence was not present in the chondrites.

In this study we analyzed three aqueously altered chondrites: Orgueil (CI1), NWA6216 (CR2), and Murray (CM2). As seen in Fig. 12, the SBC in a chondrite is expected to have a higher $\delta^{37}\text{Cl}$ value than an associated fluid (Ransom et al., 1995). This will cause the $\delta^{37}\text{Cl}_{\text{SBC}}$ value to increase following alteration. Salts that later precipitate from this fluid will also have higher $\delta^{37}\text{Cl}$ values than the fluid but to a lesser extent than the silicates (Eggenkamp et al., 1995; Schauble et al., 2003). Therefore, the SBC in

aqueously altered chondrites should have $\delta^{37}\text{Cl}$ values that are higher than that of their corresponding WSC. Both Murray and NWA6216 follow the expected trend of greater $\delta^{37}\text{Cl}_{\text{SBC}}$ values than $\delta^{37}\text{Cl}_{\text{WSC}}$ values, but Orgueil displays the opposite trend (Fig. 13). The variability in $\delta^{37}\text{Cl}_{\text{SBC}}$ values of Orgueil (Table 4, Fig.6) may be the result of fractionations that occurred after it fell on Earth. Salt mobilization may have occurred during storage as a result of interaction with the Earth's atmosphere, as observed in sulfate vein growth (Gounelle and Zolensky, 2001). We do see an increase in Cl concentration with decreasing petrologic type (type 2 to 1), i.e. with increasing degree of aqueous alteration, which is consistent with addition of Cl during alteration (Table 4, Fig.4). However, these elevated Cl concentrations may not be the result of introduction during aqueous alteration, but could also be the result of original high volatile components. Differences in $\delta^{37}\text{Cl}$ values of the C2 and C1 chondrites could also be the result of different sources of fluid and/ or fluids with different $\delta^{37}\text{Cl}$ values, with positive $\delta^{37}\text{Cl}$ fluids for CR and CM and negative $\delta^{37}\text{Cl}$ fluids for CI. During aqueous alteration, the chondrites experienced relatively low temperatures. The magnitude of fractionations usually increases with decreasing temperatures (Schauble et al., 2003; Sharp, 2007). Therefore, the $\delta^{37}\text{Cl}$ values may be a result of larger fractionations at low temperature.

Metamorphosed samples— Types 4 to 7

Metamorphic temperatures experienced by chondrites range from about 600 to 700°C for type 4, 700 to 750°C for type 5, and 750 to 950°C for type 6. At around 950°C, chondrite material will begin to melt so this is used as the cut off for solid-state metamorphism (McSween et al., 1988). The type 7 chondrite discussed in this study,

Itqiy, probably experienced some partial melting (Patzner et al., 2001) and will thus have a metamorphic temperature around 950°C and higher.

We analyzed thermally metamorphosed chondrites from each class: C, O, and E. These included Karoonda (CK4), Zag (H3-6), Bjurböle (L/LL4), Tuxtuac (LL5), Sulagiri (LL6), Saint-Séverin (LL6), Abee (EH4), Itqiy (EH7), Eagle (EL6), and Yilmia (EL6). There are two possible fractionations that can change the $\delta^{37}\text{Cl}$ value of chondrites during metamorphism as a result of volatilization and recrystallization: kinetic and equilibrium fractionation, which would cause the $\delta^{37}\text{Cl}$ value of the chondrite to increase or decrease, respectively (Fig. 12). Therefore, the SBC in metamorphosed chondrites can either have a higher or lower $\delta^{37}\text{Cl}$ value than it had before metamorphism. Samples with $\delta^{37}\text{Cl}_{\text{SBC}}$ values that are greater than the type 3 average of -0.3‰ fit with loss of ^{35}Cl during metamorphism. These include Yilmia, Eagle, Abee, and Tuxtuac (Fig. 13). Itqiy and Saint-Séverin have $\delta^{37}\text{Cl}_{\text{SBC}}$ values less than the type 3 average, consistent with loss of ^{37}Cl . Average $\delta^{37}\text{Cl}_{\text{SBC}}$ values for Sulagiri, Bjurböle, Zag, and Karoonda are all indistinguishable from the type 3 average, which may mean that metamorphism did not greatly affect the $\delta^{37}\text{Cl}_{\text{SBC}}$ values of these chondrites. There is an increase in $\delta^{37}\text{Cl}_{\text{SBC}}$ as petrologic type increases from LL3.6 to LL4 to LL5, -4.09‰ to -0.68‰ to 0.78‰, and then a decrease in $\delta^{37}\text{Cl}_{\text{SBC}}$ from LL5 to LL6, 0.78‰ to -0.33‰ and 1.10‰ (Fig. 14). However, given the small size of the data set, we are unsure if these values are significant.

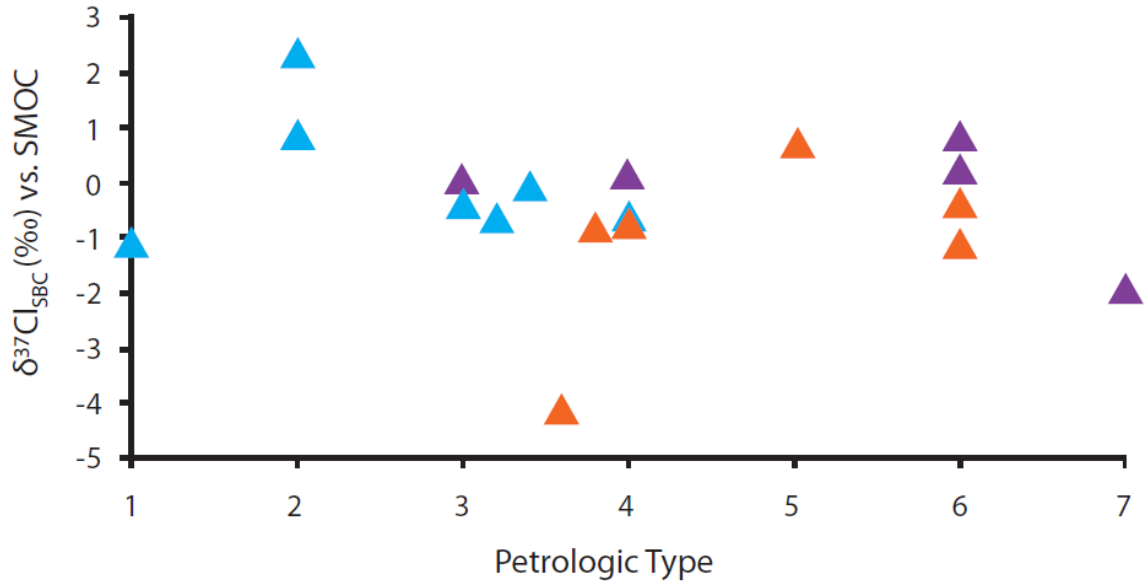


Figure 14: Mean $\delta^{37}\text{Cl}_{\text{SBC}}$ values plotted against petrologic type with same color scheme as in Fig. 1

Outlier: Parnallee LL3.6

All type 3 chondrites analyzed in this study have similar $\delta^{37}\text{Cl}$ values except Parnallee. Parnallee has the lowest $\delta^{37}\text{Cl}$ value of any of the analyzed samples, averaging -4.1 (Table 4). We measured Parnallee three times to get an average of -4.1‰ with a standard deviation of 0.1‰. Referring to the fractionation schematic in Fig. 12, we would expect the lowest $\delta^{37}\text{Cl}$ values are for HCl gas that has already partially condensed out HCl hydrate (Schauble and Sharp, 2011). We propose that a parcel of HCl gas condensed out HCl hydrate in a cold region of the nebula, ~140-160 K, and was then transported to an area of the nebula where chondrules and matrix from Parnallee were forming. However, one problem in this argument is that we do not see these low $\delta^{37}\text{Cl}$ values in any other sample. Possible explanations as to why we do not observe this fractionation in other chondrites include the following: 1) we have yet to analyze those samples that experienced the same interactions as Parnallee, 2) the very low $\delta^{37}\text{Cl}$ signature was erased

during secondary processing leaving a sample with only a slightly negative $\delta^{37}\text{Cl}$ value. Although no studies have observed direct evidence for an influx of HCl into the chondrules of Parnallee, one study has found Na and Cl-rich mesostasis in chondrules of both Parnallee (LL3.6) and Chainpur (LL3.4) (Bridges et al., 1997). Bridges et al. (1997) do not see any evidence for influx of Cl from the outside of the chondrule and instead conclude that the glassy Cl-bearing mesostasis crystallized from the residual chondrule melt. We investigated a Parnallee thin section from the UNM meteorite collection (UNM1018) and found one chondrule that had Cl-rich mesostasis around the chondrule edge, which may indicate influx of Cl from the outside of the chondrule. It is also possible that Chainpur has a similar low $\delta^{37}\text{Cl}$ value, and some chondrules from both these chondrites formed in the same region. These are questions to be investigated further.

Water Soluble Chlorides - Leachates

Leachates represent the water-soluble chlorides present in a sample, which can include salts like NaCl and FeCl_2 . These salts may have precipitated from a fluid during aqueous alteration or could be original nebular condensates. For carbonaceous chondrites, as the petrologic type decreases from 3 to 2, there is an increase in the abundance of the leachate and the Cl concentration of the leachate (Fig. 15 and 16). However, the difference is small and type 3 and 2 chondrites are from different chondrite groups making it difficult to make comparisons. For most chondrites analyzed, the WSC contributes less than 50% chlorine to the bulk composition except for Qingzhen (Fig. 15). The high Cl concentration of the leachate in Qingzhen is assumed to be from the presence

of salts, such as FeCl_2 , which have been observed in Indarch (EH4) (Rubin and Choi, 2009). For the enstatite chondrites, with increasing petrologic type there is a decrease in Cl concentration of both the WSC and SBC from 567 to 30 ppm and 510 to 23 ppm, from types 3 to 6 and 3 to 7, respectively (Table 4 and Fig. 16). Comparing the SBC and WSC Cl concentrations for each of the E chondrites, it is clear that both are decreasing with increasing petrologic type but the WSC concentrations are decreasing more significantly than SBC with WSC concentrations dropping below 100 ppm in types 6 and 7 (Table 4). This relationship could signify that during metamorphism in E chondrites, the bulk Cl concentration is most significantly affected by the loss of WSC than SBC.

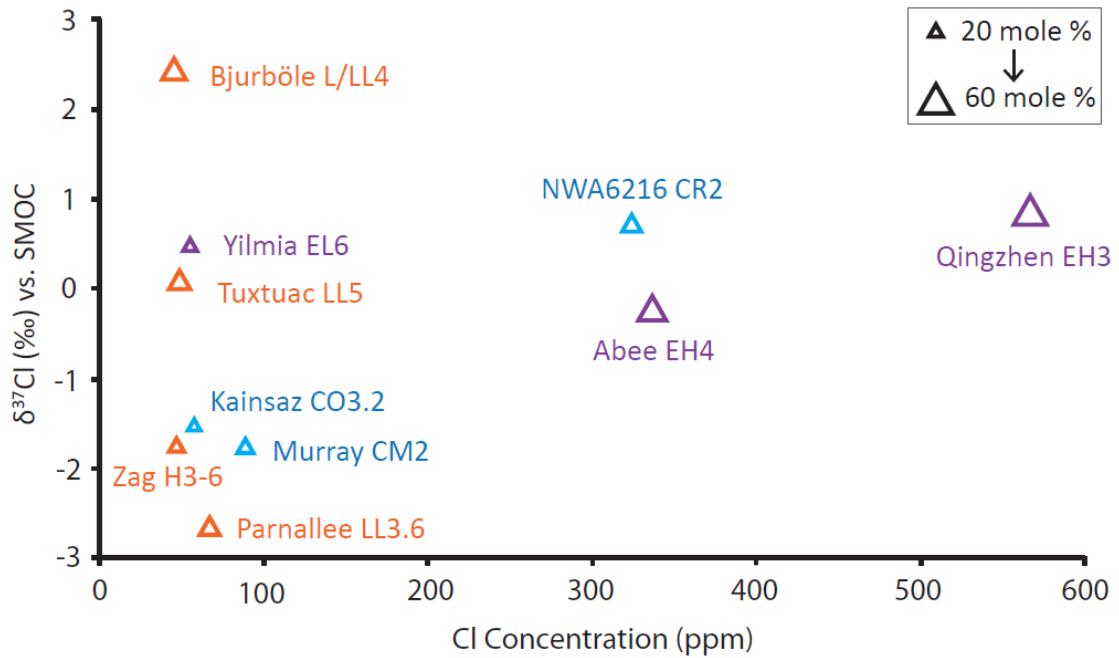


Figure 15: $\delta^{37}\text{Cl}_{\text{WSC}}$ value versus the WSC chlorine concentration with same color scheme as in Fig. 1. Size of the symbols corresponds to the mole fraction of WSC in total Cl.

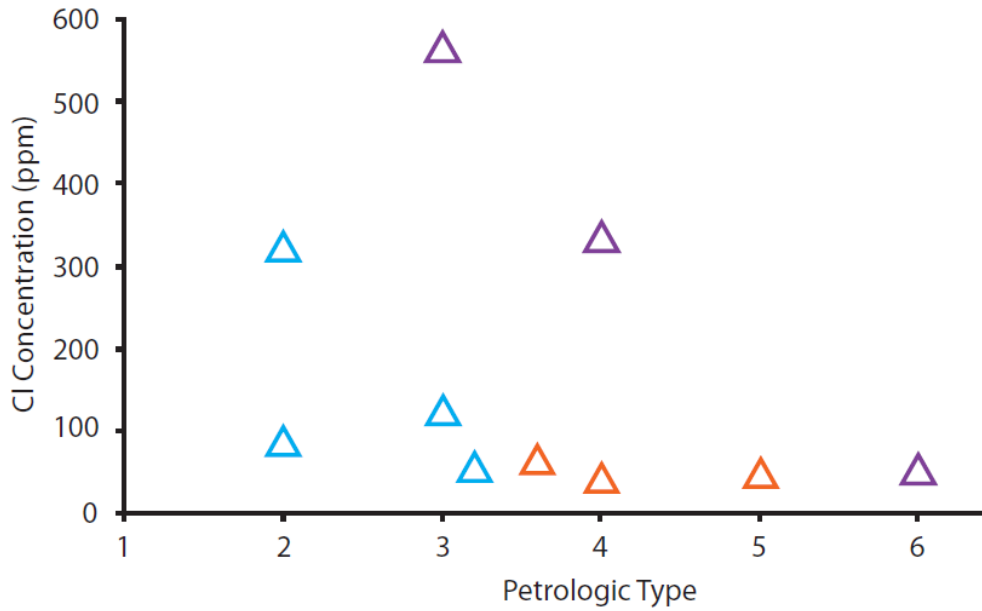


Figure 16: WSC Cl concentration versus petrologic type with same color scheme as in Fig. 1

Some leachates have higher $\delta^{37}\text{Cl}$ values than the corresponding SBC of the samples and others have lower $\delta^{37}\text{Cl}$ values (Fig. 13). Splitting the samples up according to whether they have experienced metamorphism (petrologic types 4-6), aqueous alteration (petrologic types 1,2), or are unaltered (petrologic type 3) trends begin to develop between the $\delta^{37}\text{Cl}_{\text{WSC}}$ values and the $\delta^{37}\text{Cl}_{\text{SBC}}$ values. On a plot of $\delta^{37}\text{Cl}_{\text{SBC}}$ versus $\delta^{37}\text{Cl}_{\text{WSC}}$ values (Fig. 17), a line with a slope of 1 passing through the origin would indicate that no fractionation is occurring between the SBC and the WSC. However, neither the metamorphosed nor the aqueously altered samples have a slope of 1 that passes through the origin. Correlations between the $\delta^{37}\text{Cl}_{\text{WSC}}$ values and the $\delta^{37}\text{Cl}_{\text{SBC}}$ values signify relationships between the WSC and SBC. In the case of the aqueously altered samples, the best-fit line is only between two points so we cannot consider this a correlation. One possibility for the correlation seen for the metamorphosed samples is that the fluid that precipitated the WSC also influenced the $\delta^{37}\text{Cl}_{\text{SBC}}$ values. For the unaltered

samples, if we ignore Parnallee, the $\delta^{37}\text{Cl}_{\text{WSC}}$ and the $\delta^{37}\text{Cl}_{\text{SBC}}$ values fall near 0. The greater $\delta^{37}\text{Cl}$ values of the SBC in the aqueously altered samples may indicate that during relatively low temperature alteration, ^{37}Cl is preferentially fractionated into the SBC, which is consistent with studies on terrestrial samples (Fig. 12) (Eggenkamp et al., 1995; Ransom et al., 1995). For the metamorphosed samples, the difference between the $\delta^{37}\text{Cl}_{\text{SBC}}$ and $\delta^{37}\text{Cl}_{\text{WSC}}$, $\Delta^{37}\text{Cl}_{\text{SBC-WSC}}$, is small and near zero (Table 4). The difference between the $\Delta^{37}\text{Cl}_{\text{SBC-WSC}}$ of aqueously altered and metamorphosed samples may indicate that the magnitude of fractionation between SBC and WSC is decreasing with increasing temperature.

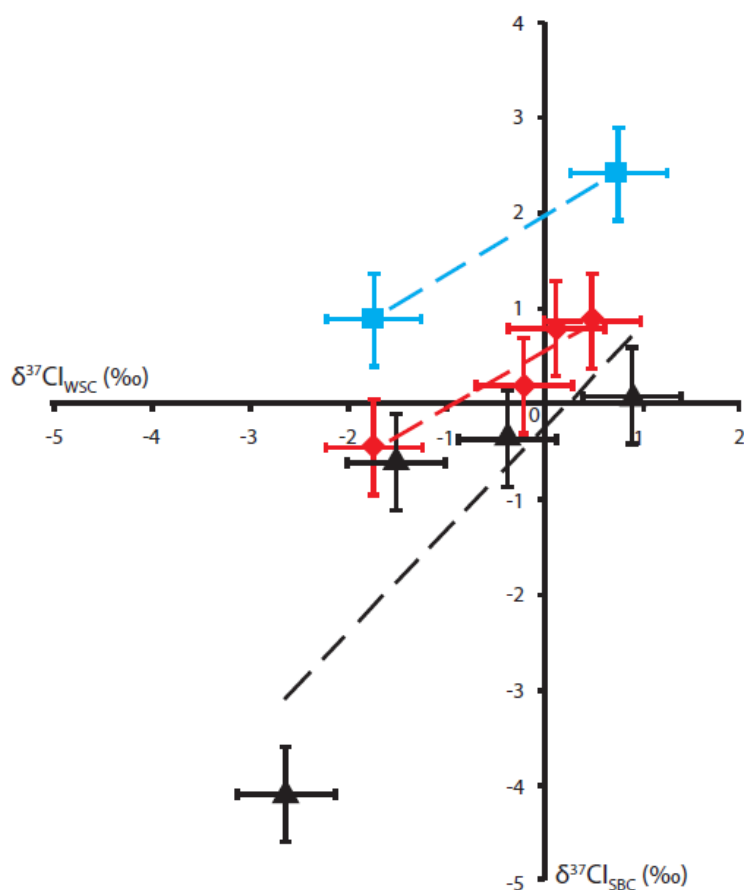


Figure 17: Mean $\delta^{37}\text{Cl}_{\text{SBC}}$ versus mean $\delta^{37}\text{Cl}_{\text{WSC}}$ values of chondrites studied. Petrologic type 3 chondrites are black triangles, type 4-6 are red diamonds, and type 1-2 are blue squares. Slopes through the groups represent best-fit linear regressions. R^2 values for metamorphosed samples (types 4-6) and type 3 samples are 0.93 and 0.72 respectively.

SIMS Data

By analyzing individual Cl-bearing phases in chondrites, we hoped to understand the relationship between the $\delta^{37}\text{Cl}_{\text{WSC}}$ and $\delta^{37}\text{Cl}_{\text{SBC}}$ values and the $\delta^{37}\text{Cl}$ value of individual grains that we believe most likely represent the dominant Cl-bearing phase in the chondrite. The $\delta^{37}\text{Cl}_{\text{SBC}}$ value should be similar to the $\delta^{37}\text{Cl}$ value of the Cl-bearing phases, Cl-apatite in O chondrites and chondrule mesostasis and djerfisherite in Qingzhen. A study of the distribution of Cl in ordinary chondrites found that in lower

petrologic types, 3.0 to 3.7, the dominant Cl-bearing phases are feldspathoids such as sodalite and scapolite while in higher petrologic types apatite becomes the dominant phase (Kimura and Ikeda, 1997). However, we did not observe this relationship. For the samples for which we measured $\delta^{37}\text{Cl}_{\text{WSC}}$ and $\delta^{37}\text{Cl}_{\text{SBC}}$ values, Zag, Bjurböle, Tuxtuac, and Qingzhen the $\delta^{37}\text{Cl}_{\text{SBC}}$ value was intermediate between the $\delta^{37}\text{Cl}_{\text{WSC}}$ value and the $\delta^{37}\text{Cl}$ values of the individual grains (Fig. 11), with the exception of one analysis for Qingzhen. For these samples, we interpreted this to mean that the SBC was actually a mixture of the WSC and Cl-bearing phases. It is possible that when the samples were rinsed, not all of the WSC was leached since some samples were difficult to crush into a fine powder. If we had been able to measure the $\delta^{37}\text{Cl}_{\text{WSC}}$ value of Saint-Séverin, we may have seen a similar trend. Another possibility for the SBC having an intermediate $\delta^{37}\text{Cl}$ value is that the Cl-bearing phase analyzed is not the only SBC Cl carrier in the sample. We do not have a mechanism to explain the large variation in $\delta^{37}\text{Cl}$ values for Cl-apatite grains in Zag, Tuxtuac, or Saint-Séverin. For Zag, one possibility that could explain the variation in $\delta^{37}\text{Cl}$ values is apatite grain growth from evolving Cl-rich dry fluids on the Zag chondrite parent body (Jones et al., 2011a).

In a more detailed study on the Qingzhen chondrules (Mercer et al., in progress), we concluded that the Cl in the mesostases was primary and was present in the chondrule precursor assemblage. We would assume that this primary Cl-bearing mesostasis would closely match the $\delta^{37}\text{Cl}_{\text{SBC}}$ values of type 3 chondritic materials because Qingzhen is a petrologic type 3 chondrite. The $\delta^{37}\text{Cl}$ values of the chondrule mesostases and djerfisherite cover the same range except for one point (1.3‰) (Fig. 11). The mean of the chondrule mesostases is $-0.9 \pm 1.0\text{‰}$. With large error bars (Fig. 11), we cannot say for

sure that the chondrule mesostasis is the same as the average $\delta^{37}\text{Cl}$ value for type 3 chondrites, but the type 3 average value, $-0.3 \pm 0.4\text{‰}$, falls within the range of SIMS values.

Earth

By studying the chlorine isotope composition of chondrites, we have determined that there was one chlorine isotope reservoir in the chondrite-forming region, with a $\delta^{37}\text{Cl}$ value of around -0.3‰ . We have also observed how some secondary processes that took place on chondrite parent bodies can affect the $\delta^{37}\text{Cl}$ value. Analyses of chondrites can also help us understand the $\delta^{37}\text{Cl}$ value of the Earth's mantle because chondritic material is assumed to have formed the Earth, since elemental abundances of the bulk silicate Earth most closely match carbonaceous chondrites (e.g. Schönbachler et al., 2010).

Chlorine isotope studies of mantle materials such as mid ocean ridge basalts (MORB), peridotites, kimberlites, rift basalts, and mantle plume basalts have found that the $\delta^{37}\text{Cl}$ value of the mantle is $-0.15 \pm 0.35\text{‰}$ (Sharp et al., 2007, 2010b, 2011b). This value is indistinguishable from the chondritic type 3 average of $-0.3 \pm 0.4\text{‰}$. However, other published data for the $\delta^{37}\text{Cl}$ value of the mantle are different. Analyses of MORB samples by gas source mass spectrometry by Boniface et al. (2008) yield $\delta^{37}\text{Cl}$ values less than -1.6‰ . Layne et al. (2009) using SIMS measured negative $\delta^{37}\text{Cl}$ values on an archival MORB. These authors concluded that the mantle had a $\delta^{37}\text{Cl}$ value less than -3.0‰ (Layne et al., 2009).

One key difference between the work of Sharp et al. (2007, 2010b, 2011b) and this study with the studies which have measured low $\delta^{37}\text{Cl}$ values is the measurement of

samples with very low Cl content. We conducted a test on the effect sample size has on the $\delta^{37}\text{Cl}$ values of a basalt sample. We observed a steep drop off to more negative $\delta^{37}\text{Cl}$ values when a sample with a low Cl content was measured. In the case of Bonifacie et al. (2008), some of the MORB samples measured had very low Cl contents, on the order of 50 ppm Cl. The $\delta^{37}\text{Cl}$ values of these samples were also measured differently in a different laboratory (M. Bonifacie, personal communication, 2011). We conclude that for low sample sizes, the measured $\delta^{37}\text{Cl}$ values are not reliable. We therefore suggest the presence of one homogeneous chlorine isotope reservoir in the inner solar system based on the similarity of the $\delta^{37}\text{Cl}$ values of type 3 chondritic materials, crustal, and mantle materials measured in this study and by Sharp et al. (2007, 2010b, 2011b).

5: CONCLUSIONS

Using the gas source IRMS we have shown that the $\delta^{37}\text{Cl}_{\text{SBC}}$ value of unaltered chondrites, petrologic type 3, from the C, O, and E classes is constant at $-0.3 \pm 0.4\%$. This indicates the presence of a single homogeneous chlorine isotope reservoir in the inner solar nebula. The similarity of this reservoir to the $\delta^{37}\text{Cl}$ values of the bulk Earth, the lowest value obtained for the Moon, and the average of martian meteorite samples obtained in other studies further reinforces this conclusion. Using this value as a benchmark, investigation of altered chondrite samples has shown that $\delta^{37}\text{Cl}$ values and Cl concentration of the SBC and WSC can change during aqueous alteration and metamorphism. However, we observed that secondary processes that occurred on the chondrite parent bodies have not significantly changed the $\delta^{37}\text{Cl}$ values, but in some cases have greatly affected the Cl concentration. Finally, we observed that the average $\delta^{37}\text{Cl}$ value of the type 3 chondrites is indistinguishable from measurements of mantle samples from the Earth, $-0.15 \pm 0.35\%$.

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