Ca AND Ti ISOTOPIC RATIOS IN HIGH-DENSITY GRAPHITE GRAINS FROM ORGUEIL.

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Introduction: In a previous study [1], we reported C, N, O and Si isotopic analyses of high-density graphite grains from Orgueil. Some of the grains from the ORG1f, 1g and 1i density fractions ($\rho \sim 2.02$-2.04, 2.04-2.12, and 2.16-2.30 g cm^{-3}, respectively) were found to be highly enriched in ^{30}Si and ^{12}C. We suggested that these grains originated from low-metallicity AGB stars that did not experience any cool bottom processing [1, 2].

In a continuing effort to better understand high-density graphite grains, we measured C, N, O, Si, Al-Mg, K, Ca, and Ti isotopes of a new set of grains from the ORG1f density fraction. We also expect to be able to analyze the same grains for heavy element isotopes (Sr, Zr, Mo, Ru, Ba) by resonant ionization mass spectrometry (RIMS) with CHARISMA. High-density graphite grains from Orgueil are ideal for such extensive isotopic studies because they are fairly large (average size of the grains in the present study ~ 5 µm) and, hence, do not sputter away and will last for the entire study. High-density grains from Murchison were found to contain subgrains rich in the s-process elements Zr, Mo, and Ru [3]. These elements are predicted to be highly abundant in the envelope of AGB stars [4]. A distinct disadvantage, though, is that high-density grains contain very low concentrations of trace elements, making high precision measurements of their isotopes challenging.

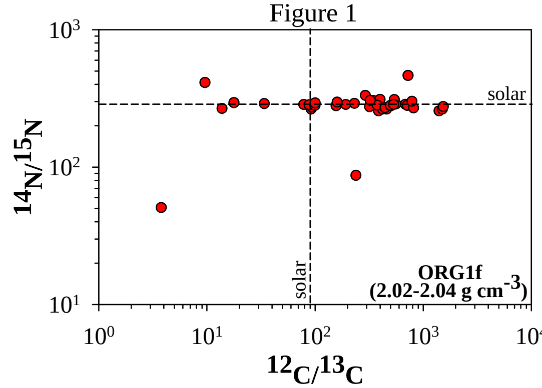
We present here the results of our isotopic analyses on the high density fraction ORG1f. We will focus on the K, Ca, and Ti results that force us to re-evaluate the stellar sources of some these grains.

Experimental Methods: Forty-four spherical, carbonaceous grains were identified by X-ray analysis in the SEM and then picked with a micromanipulator and deposited on a gold-foil mount. This procedure was essential to isolate the grains from the large amounts of macromolecular carbonaceous material, in which graphite grains from Orgueil are often found embedded. It reduces contamination from the surrounding material and will also make it easier to locate the grains for future RIMS analysis. After mounting the grains, we coated the mount with a thin (~ 10 nm) layer of gold to prevent the grains from falling off.

The isotopic measurements of these grains were carried out with the NanoSIMS. We used a Cs$^+$ primary beam to generate negative secondary ions of ^{12}C, ^{13}C, ^{16}O, and ^{18}O in phase 1 of the analyses, and of ^{12}C^{14}N, ^{12}C^{15}N, ^{28}Si, ^{29}Si and ^{30}Si in phase 2. These ions were counted in multidetection mode. In phase 3 of the analyses, positive secondary ions of ^{12}C, ^{24}Mg, ^{25}Mg and ^{27}Al, produced with an O$^-$ beam, were detected. The K, Ca, and Ti measurements were carried out with the O$^-$ beam in a combination of peak-jumping and multidetection modes. Positive secondary ions of ^{39}K, ^{41}K and ^{43}Ca (B field 1) and ^{12}C, ^{40}Ca, ^{42}Ca, ^{44}Ca and ^{48}Ti (B field 2) were measured to obtain K and Ca ratios. Ti isotopes were measured using 3 magnetic fields: at B1 we detected – ^{46}Ti, ^{48}Ti, and ^{50}Ti; B2 – ^{47}Ti, ^{49}Ti, and ^{51}V; and B3 – ^{12}C, ^{40}Ca, ^{48}Ti, ^{50}Ti, and ^{52}Cr. ^{51}V and ^{52}Cr were used to correct the ^{50}Ti signal for isobaric interferences from V and Cr, and, ^{40}Ca was measured to correct for Ca interferences at masses 46 and 48.

Results and Discussion: *C, N, O, Si, and Al-Mg isotopes*: The ^{12}C/^{13}C ratios cover a similar large range (4-1500) as seen in previous studies (Figure 1) [1]. Most grains contain isotopically light carbon but a few have ^{12}C/^{13}C ratios between 4 and 20. In accordance with previous results obtained on Orgueil and Murchison high-density grains [1, 5], most of the grains have isotopically normal N (Figure 1) and O ratios. Two grains were found to be enriched in ^{15}N and two depleted. Only one grain has an anomalous ^{16}O/^{18}O ratio of ~ 600 (Solar ^{16}O/^{18}O ~ 499), the rest are all normal. This puzzling result in view of the large range of ^{12}C/^{13}C ratios seen in these grains has been explained as equilibration with normal N and O, either on the parent body or in the laboratory [5]. The Si isotopes show a similar behaviour. Apart from some large anomalies in a few grains, most of the grains have small anomalies or have normal $\delta^{29,30}$Si/^{28}Si values. The largest anomalies were seen in one grain, g-o68, that has δ^{29}Si = 1341 ‰ and δ^{30}Si = 896 ‰. This grain is enriched in ^{12}C (^{12}C/^{13}C ~ 239). Similarly, we found only a few grains with ^{25,26}Mg excesses. The largest δ^{25}Mg value obtained was 115 ‰. Grain g-o67 has the largest ^{26}Mg excess (δ^{26}Mg = 1593 ‰). This grain consequently has a large inferred ^{26}Al/^{27}Al ratio of 0.01. The typical ^{26}Al/^{27}Al ratio expected in AGB stars

Figure 1



is 0.001. Five grains have inferred $^{26}Al/^{27}Al$ ratios on the order of 10^{-4}. The Al/Mg ratios for most of the remaining grains were very low so that even if these grains had $^{26}Al/^{27}Al$ ratios typical of AGB stars we would not be able to detect the resulting ^{26}Mg excesses. There is a possibility that the equilibration processes affecting the N and O also dilute the Si and Mg isotopes in these high-density grains.

K, Ca, and Ti isotopes: Table 1 lists the C, Ca and Ti isotopic ratios of interesting grains. Most of the grains have normal $^{41}K/^{39}K$ ratios (0.072). Grains g-9, g-18, g-25, g-38 and g-o68, have high $^{41}K/^{39}K$ ratios ranging from 0.079-1.00. Since the intrinsic concentration of K in graphite grains is expected to be very low, we attribute the ^{41}K excesses to the decay of ^{41}Ca ($T_{1/2} = 1.03\times10^5$ a) [6]. The inferred $^{41}Ca/^{40}Ca$ ratios in Table 1 range up to 0.01. The $^{41}Ca/^{40}Ca$ ratios expected in AGB stars are on the order of 10^{-4} to 10^{-5}. Grains g-9, g-18, g-25, g-o68 have $^{41}Ca/^{40}Ca$ ratios that are incompatible with an AGB origin. The highest of these ratios can be obtained in the He/C, C/O and O-rich zones of Type II supernovae where the $^{13}C(\alpha,n)^{16}O$ and $^{22}Ne(\alpha,n)^{25}Mg$ reactions provide ample neutrons for the production of ^{41}Ca [7]. However, the $^{41}K/^{39}K$ ratio is expected to be around 0.2 in the He/C zone, and can be as high as 0.4 in the C/O zone, which does not explain some of the highest values seen in our grains. Three of the grains with the highest $^{41}Ca/^{40}Ca$ values (g-18, g-25 and g-o68) have high $^{12}C/^{13}C$ ratios, which is compatible with a SN origin. Grain g-o68 has an additional SN signature of being ^{15}N enriched ($^{14}N/^{15}N \sim 87$). But g-9 has a low $^{12}C/^{13}C$ ratio. The very high $\delta^{42,43,44}Ca$ values for this and several other grains are completely incompatible with an AGB star origin. No AGB model can synthesize such high ratios, which instead are in the range of those predicted for the O/Si, O/Ne, and O/C zones of Type II SNe. Except for g-o68, all of these grains have $^{12}C/^{13}C < 20$. However, in all these SN zones O >> C and $^{12}C/^{13}C$ ratios are extremely high. ^{44}Ca excesses that are comparable to the $^{42,43}Ca$ excesses can be explained by neutron capture, but in grains g-1, g-25, g-38, g-o67, the large ^{44}Ca excesses must be the result of the decay of ^{44}Ti ($T_{1/2} = 60$ a). ^{44}Ti is only produced by α-rich freezeout in the Ni/Si zones of Type II SNe [8]. However, only g-25 has a high $^{12}C/^{13}C$ ratio expected for a SN origin, while the other three grains have low $^{12}C/^{13}C$ ratios. A similar signature was observed in SiC grains with very low $^{12}C/^{13}C$ and $^{14}N/^{15}N$ ratios by Nittler and Hoppe [9]. Similar to the $^{42,43,44}Ca$ excesses, $^{46,47,49,50}Ti$ excesses in several grains are much higher than predicted for AGB stars and approach those predicted for O-rich SN zones. Grain g-9 also has extreme enrichments in the Ti isotopes, but some of the ^{46}Ti excess could be from anomalous ^{46}Ca.

Conclusions: The measurements of new isotopic systems on high-density graphite grains lead us to consider Type II supernovae as the stellar sources of some of the grains. Four grains with high $^{12}C/^{13}C$ ratios show SN signatures in their $^{41}Ca/^{40}Ca$, $^{44}Ti/^{48}Ti$ and other Ti isotopic ratios. What presents a puzzle are the grains with extreme Ca and Ti isotopic anomalies, which indicate a SN origin, but have $^{12}C/^{13}C < 20$. The very low $^{12}C/^{13}C$ ratios of these alleged SN grains remain a mystery. No stellar sources for this population have yet been identified. We need to measure more isotopic systems in order to better constrain the stellar sources. These findings undoubtedly present a new challenge to nucleosynthesis models.

References: [1] Jadhav M. et al. (2006) *New Astron. Rev. 50*, 591–595. [2] Zinner E. et al. (2006) *PoS. (NIC-IX)* 019. [3] Croat T. K. et al. (2005) *ApJ 631*, 976-987. [4] Lugaro M. et al. (2003) *ApJ 593*, 486-508. [5] Zinner E. et al. (1995) *Meteoritics 30*, 209-226. [6] Amari S. et al. (1996) *ApJ 470*, L101-L104. [7] Woosley S. E. and Weaver T. A. (1995) *ApJS* 101, 181-235. [8] Timmes F. X. (1996) *ApJ* 464, 332-341. [9] Nittler L. R. and Hoppe P. (2005) *ApJ 631*, L89-L92.

Table 1: C, Ca and Ti isotopic ratios of high-density graphite grains from ORG1f

Grain	$^{12}C/^{13}C$	$^{41}Ca/^{40}Ca$ (x10^{-3})	$\delta^{42}Ca/^{40}Ca$ (‰)	$\delta^{43}Ca/^{40}Ca$ (‰)	$\delta^{44}Ca/^{40}Ca$ (‰)	$^{44}Ti/^{48}Ti$ (x10^{-3})	$\delta^{46}Ti/^{48}Ti$ (‰)	$\delta^{47}Ti/^{48}Ti$ (‰)	$\delta^{49}Ti/^{48}Ti$ (‰)	$\delta^{50}Ti/^{48}Ti$ (‰)
g-1	14	0.3 ± 0.9	-152 ± 96	156 ± 239	6018 ± 203	0.179 ± 0.008	-15 ± 8	-28 ± 9	161 ± 11	44 ± 15
g-9	18	2.3 ± 0.4	16028 ± 316	27641 ± 805	9396 ± 151	c	35032 ± 4432	1376 ± 371	2278 ± 298	32827 ± 4594
g-13	816	0.6 ± 0.4	77 ± 48	142 ± 104	157 ± 30	c	613 ± 116	318 ± 129	966 ± 209	b
g-18	1507	10.6 ± 0.3	992 ± 58	4057 ± 201	2042 ± 46	c	522 ± 98	2119 ± 354	2648 ± 204	b
g-21	461	a	-42 ± 46	48 ± 103	-13 ± 28	c	387 ± 66	80 ± 59	679 ± 123	1722 ± 337
g-25	725	6.0 ± 0.2	93 ± 22	90 ± 42	1584 ± 26	0.970 ± 0.073	58 ± 5	-32 ± 12	754 ± 20	214 ± 23
g-29	10	0.2 ± 0.2	1451 ± 50	1628 ± 100	540 ± 24	c	d	d	d	d
g-33	560	a	-5 ± 58	9 ± 122	104 ± 37	c	477 ± 24	97 ± 27	1237 ± 38	2621 ± 296
g-34	8	0.1 ± 0.1	5064 ± 60	7410 ± 146	2179 ± 25	c	d	d	d	d
g-38	4	1.2 ± 1.2	-118 ± 177	-602 ± 274	51886 ± 1499	0.765 ± 0.028	-77 ± 12	-98 ± 15	125 ± 6	242 ± 6
g-39	324	0.6 ± 0.4	21 ± 38	-30 ± 79	-19 ± 22	c	285 ± 100	78 ± 79	614 ± 64	4224 ± 1568
g-40	11	0.2 ± 0.3	3375 ± 65	3662 ± 138	554 ± 22	c	d	d	d	d
g-o65	533	a	340 ± 120	294 ± 252	26 ± 63	c	1180 ± 30	310 ± 20	1798 ± 37	7416 ± 154
g-o67	4	0.3 ± 0.3	63 ± 52	15 ± 107	3767 ± 77	0.595 ± 0.025	2 ± 4	14 ± 4	169 ± 5	236 ± 6
g-o68	239	10.2 ± 0.0	996 ± 13	2839 ± 41	289 ± 7	c	1975 ± 160	327 ± 98	1562 ± 169	2184 ± 329

Note: Errors are 1 σ; δ values are deviations from solar ratios per mil

a The Ca/K ratios for these grains were very low, making it impossible to derive a meaningful $^{41}Ca/^{40}Ca$ ratio from the ^{41}K excess.

b Not reported, because the ^{50}Cr contribution to the ion signal of these grains was calculated to be ~ 60%, increasing the uncertainty of the results.

c Did not derive $^{44}Ti/^{48}Ti$ ratios for these grains because the $\delta^{44}Ca/^{40}Ca$ values are comparable to the $\delta^{42}Ca/^{40}Ca$ and $\delta^{43}Ca/^{40}Ca$ values.

d Not measured because of very low Ti signals.