

Incorporation of Short-Lived ^{10}Be in a Calcium-Aluminum-Rich Inclusion from the Allende Meteorite

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Enrichments in boron-10/boron-11 in a calcium-aluminum-rich inclusion from the Allende carbonaceous chondrite are correlated with beryllium/boron in a manner indicative of the in situ decay of short-lived beryllium-10. Because this radionuclide is produced only by nuclear spallation reactions, its existence in early solar system materials attests to intense irradiation processes in the solar nebula. The particle fluence inferred from the initial beryllium-10/beryllium-9 is sufficient to produce other short-lived nuclides, calcium-41 and manganese-53, found in meteorites, but the high canonical abundance of aluminum-26 may still require seeding of the solar system by radioactive stellar debris.

When the oldest solar system materials, the Ca-Al-rich inclusions (CAIs) of primitive chondrite meteorites (1), first crystallized in the solar nebula, their major elements included small concentrations of short-lived radioactive isotopes. Evidence for the in situ decay of now extinct ^{26}Al [half-life ($\tau_{1/2}$) = 0.7 million years (My)] and ^{41}Ca ($\tau_{1/2}$ = 0.1 My) in CAI minerals is provided by excesses of their respective daughter products, which are correlated with the relative abundance of a stable isotope of the parent element. The origins of these and other (2) relatively short-lived radionuclides found in meteorites are controversial: These isotopes can be produced by nucleosynthesis in different stellar environments (3), or they may be the products of nuclear reactions induced by the collisions of energetic particles with ambient dust or gas (4, 5). The astrophysical implications of these contrasting interpretations of extinct radioactivities are different regarding the processes and time scales inferred for the formation of the solar system (6). Here, we report evidence for the existence of an extinct radionuclide, ^{10}Be ($\tau_{1/2}$ = 1.5 My), in CAIs that indicates that primitive meteorites preserve a record of intense irradiation processes that may have occurred in the early solar system.

Unlike other elements, Be, together with Li and B, is thought to be produced predominantly by spallation reactions between galactic cosmic rays (GCRs) and the interstellar medium (7). The inefficiency of this production, coupled

with the destruction of these elements in stellar interiors by nuclear burning, accounts for the depleted cosmic abundances of Li-Be-B relative to neighboring low-mass elements (8). However, the discrepancies between the $^7\text{Li}/^6\text{Li}$ and $^{11}\text{B}/^{10}\text{B}$ ratios of the solar system ($^{11}\text{B}/^{10}\text{B}$ = 4.0 ± 0.1 and $^7\text{Li}/^6\text{Li}$ = 12.1 ± 0.1) and those inferred for interstellar production by GCR ($^{11}\text{B}/^{10}\text{B}$ \approx 2.5 and $^7\text{Li}/^6\text{Li}$ \approx 1.5) require additional nucleosynthetic sources for these elements. Spallation reactions occurring at relatively low energy (< 100 MeV per nucleon) or several stellar sources producing pure ^7Li and ^{11}B can theoretically provide the additional Li and B necessary to match their respective chondritic isotopic compositions (9).

The observed B isotopic variations in chondrules (10) have been interpreted as the result of such low-energy irradiation processes occurring in the molecular cloud that gave birth to the solar system (11). Low-energy irradiation has also been invoked to explain the presence of live ^{26}Al in CAIs. Such an irradiation could have taken place either during the quiescent phase of the protosolar nebula [e.g., (4)] or during the early phases of the sun's formation when energetic particles from magnetic reconnection flares irradiate materials at the inner edge of the protosolar accretion disk (5, 12). In addition to the stable isotopes of B and Li, the nuclear cross sections (13) are such that appreciable amounts of the radioactive isotope ^{10}Be are also expected to be produced during any such low-energy irradiation processes. We used an ion microprobe to determine Li and B isotopic compositions and Be concentrations in CAIs to search for evidence of irradiation of early solar system materials.

Three coarse-grained type B CAIs (TS-34, 3529-30, and 3529-41) from the Allende carbonaceous chondrite were investigated (14). Previous ion microprobe measurements

(15, 16) demonstrate that all three inclusions initially formed with close to canonical $^{26}\text{Al}/^{27}\text{Al}$ ratios, thus indicating their early crystallization in the solar nebula. However, detailed petrographic and isotopic studies of the latter two inclusions (15) showed that some redistribution of radiogenic ^{26}Mg occurred, probably during a secondary thermal event that resulted in alteration and recrystallization of melilite and/or anorthite. The degree of isotopic disturbance and of mineralogic alteration appears somewhat greater in 3529-30 than in 3529-41. The $^7\text{Li}/^6\text{Li}$, $^{11}\text{B}/^{10}\text{B}$, and $^9\text{Be}/^{11}\text{B}$ compositions as well as the atomic concentrations of Li, Be, and B were determined in multiple spots of each sample (Table 1) with a CAMECA ims 1270 ion microprobe (17).

Concentration ranges for Li [3 to 750 parts per billion (ppb)] and Be (50 to 3000 ppb) are comparable to, but more variable than, previous determinations in CAIs (18). Boron concentration is even more variable among the three CAIs. In two samples, B is depleted (6 to 150 ppb, with one spot at \sim 900 ppb) relative to CI concentrations, as expected on the basis of its volatility (19), but in 3529-30, B is abundant [1 to 10 parts per million (ppm)] in all spots analyzed. Beryllium is found to be preferentially concentrated in melilite in accord with previous ion probe analyses and partitioning experiments (20, 21), resulting in high Be/B ratios in melilite from 3529-41.

Among the three CAIs, Li isotope variability is limited to <50 per mil (‰), and all analyses overlap the range previously observed in chondrules (22). In contrast, B shows large $\delta^{11}\text{B}$ anomalies ranging to -410% in sample 3529-41, greatly exceeding B isotope variations reported in meteorites (22, 23). The large negative $\delta^{11}\text{B}$ values cannot be due to Rayleigh fractionation resulting from volatilization of B during CAI formation because this would result in the preferential loss of ^{10}B , opposite to the observed ^{10}B excesses. The magnitude of the anomaly also cannot be the result of an in situ spallation by GCR in the Allende meteoroid that would produce correlated ^6Li and ^{10}B excesses that are not observed.

The ^{10}B excesses in 3529-41 are correlated with Be/B (Fig. 1) in a manner indicating that short-lived ^{10}Be was incorporated into this CAI during crystallization and was preferentially partitioned into melilite where it subsequently decayed, producing radiogenic ^{10}B . The slope of the correlation line implies an initial $^{10}\text{Be}/^9\text{Be}$ ratio of $(9.5 \pm 1.9) \times 10^{-4}$, and the intercept yields an initial $^{11}\text{B}/^{10}\text{B}$ ratio = 3.93 ($\delta^{11}\text{B}$ = $-28 \pm 9\%$), which is close to the lowest value found in chondrules (22) and lower than the ratio of 4.03 ($\delta^{11}\text{B}$ = -3%) for CI chondrites (23). The other CAIs, which do not exhibit strong Be/B fractionation (24), lack sig-

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nificant ^{10}B enrichments and have $\delta^{11}\text{B}$ values in agreement with the inferred initial $^{11}\text{B}/^{10}\text{B}$ ratio of 3529-41.

Because ^{10}Be is not produced by stellar nucleosynthesis, the existence of this radioisotope in a CAI demonstrates that some early solar system materials preserve a record of irradiation processes. That the excess ^{10}B follows the crystal-chemical behavior of Be indicates that the radioactive ^{10}Be existed in the CAI melt, similar to the situation for ^{26}Al and ^{41}Ca . The presence of live ^{10}Be raises three questions related to the astrophysical implications of how CAI precursors obtained their short-lived radioactivity: What are the intensity and energy spectrum of the incident particles, where did this irradiation take place, and what are the collateral consequences of such an irradiation, e.g., with respect to other short-lived radionuclides present in the early solar system. A rigorous calculation of the fluence (Φt) necessary to yield $^{10}\text{Be}/^{9}\text{Be} = 9.5 \times 10^{-4}$ in CAI precursors requires detailed knowledge of the target composition and the energy spectrum of incident particles; however, a first-order estimate may be obtained with cross sections (13) for the nuclear reaction $^{16}\text{O}(p,x)^{10}\text{Be}$ and assuming a power law (E^{-3}) distribution in proton energy. The proton fluence ($> 20\text{MeV}$) is in the range 10^{18} to 10^{19} cm^{-2} for irradiation of targets having CAI compositions. Irradiation of solar composition material results in fluence estimates about one order of magnitude lower. All these estimates are below the upper limits set by previous Li isotope measurements of an Allende CAI (18) and slightly lower than the fluence inferred from the B isotopic variations observed in chondrules (22).

With respect to the astrophysical environment, three possible scenarios for this irradiation can be considered: (i) The ^{10}Be may have been inherited from the steady-state galactic reservoir produced by GCR, (ii) the ^{10}Be may have been produced just before collapse of the solar nebula from the interaction of energetic ejecta from a supernova explosion with the surrounding interstellar medium, or (iii) the ^{10}Be could have been locally synthesized by irradiation within the protosolar nebula by intense stellar flares, similar to those inferred from x-ray observations (25) of young stellar objects (YSOs).

An upper limit on the $^{10}\text{Be}/^{9}\text{Be}$ ratio of interstellar matter in a molecular cloud core that collapsed to form the solar nebula can be constructed from the $^9\text{Be}/\text{H}$ production rate by GCR 4.5 billion years ago (10^{-21} per year) derived from stellar observations (26), the production of ^{10}Be relative to ^9Be (~ 0.1), and the rate of ^{10}Be radioactive decay. For an initial solar $^9\text{Be}/\text{H}$ (2.6×10^{-11}), a steady state is reached after ~ 7 My with $^{10}\text{Be}/^{9}\text{Be} = 8.3 \times 10^{-6}$, which implies that only $\sim 1\%$ of the ^{10}Be found in Allende 3529-41 should be from the

galactic background. Lower energy cosmic rays (< 100 MeV per nucleon) are stopped within a molecular cloud core, in principle providing a mechanism for locally enhancing the proportion of young GCR-Be relative to old interstellar Be in the presolar molecular cloud compared with the average galactic mixing ratio discussed above. Because such GCRs have $^{10}\text{Be}/^{9}\text{Be} = 0.1$ (27), an enhancement by a factor of 100 of this mixing ratio would be necessary for local heterogeneities to develop with a $^{10}\text{Be}/^{9}\text{Be}$ ratio of ~ 0.001 . However,

mixing ratios of this order appear to be ruled out (28) to avoid overproducing other short-lived nuclides (e.g., ^{53}Mn). A supernova explosion can provide another potential source of freshly synthesized ^{10}Be from either spallation reactions occurring between C and O accelerated nuclei and ambient interstellar gas (9, 29) or nuclear reactions in shock waves (30). Although once promising, the first scenario now seems unlikely because the measured flux of γ -rays from nuclear deexcitation lines of C and O are low (31), and the second process yields

Fig. 1. Boron isotopic composition of individual minerals from Allende CAIs as a function of Be/B ratio in the same material. Error bars are 2σ . The $^{10}\text{B}/^{11}\text{B}$ values from various spots of CAI 3529-41 show ^{10}B excesses that are correlated with the Be/B ratio in a manner indicative of the in situ decay of ^{10}Be in the CAI. The slope of the correlation line (weighted fit to the data of 3529-41 only) corresponds to an initial $^{10}\text{Be}/^{9}\text{Be} = 0.00095 \pm 0.00019$ (2σ) at the time of crystallization. The intercept indicates $^{10}\text{B}/^{11}\text{B} = 0.254 \pm 0.002$, which is higher than $^{10}\text{B}/^{11}\text{B}$ for CI chondrites (23), as shown by the horizontal line. The inset shows the same data at an expanded scale; data for CAIs 3529-30 and TS-34 are consistent with the Be-B isotope systematics of 3529-41.

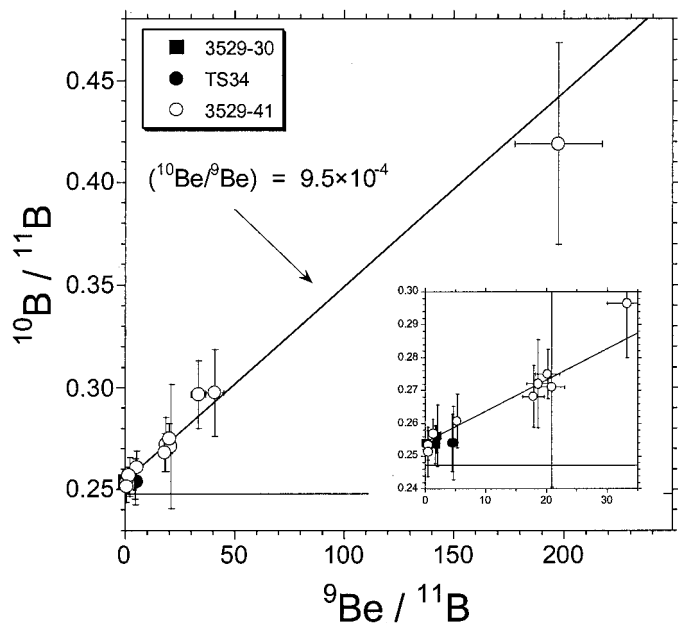


Table 1. Li and B isotopic compositions and Li-Be-B concentrations in Allende CAIs.

Phase*	$\delta^7\text{Li}$ (‰)	1 σ	$\delta^{11}\text{B}$ (‰)	1 σ	$^7\text{Li}/^{11}\text{B}$	Be/ ^{11}B	[B] ppm
<i>3529-30</i>							
mel-1	-16.4	6.3	-35.2	18.3	0.73	2.05	1.02
mel-1,1	-0.9	4.8	-24.9	11.5	0.67	1.67	1.98
mel-3	-13.6	4.7	-31.0	8.0	0.51	1.84	2.26
alt	-0.6	2.1	-26.7	1.3	0.07	0.06	10.2
<i>TS-34</i>							
mel-1	-19.6	8.3	-51.5	16.7	1.00	4.47	0.135
mel-2	-60.4	31.0	-14.0	22.4	0.16	4.64	0.034
<i>3529-41</i>							
mel-1	-3.9	3.0	-91.6	24.6	9.84	18.6	0.097
mel-1,1	1.8	7.7	-88.4	56.4	11.5	20.9	0.056
mel-2	1.0	3.6	-166.5	28.0	7.66	33.3	0.067
spinel	8.5	3.7	-24.2	9.0	2.36	0.49	n.d.
mel-4	0.8	5.5	-51.8	15.7	1.67	5.28	0.135
mel-5	-3.1	5.1	-38.1	8.1	0.59	1.26	0.927
mel-6	-11.5	3.6	-168.8	35.9	20.9	40.8	0.279
mel-7	-37.9	25.5	-101.3	13.6	0.07	20.2	0.153
mel-7,1	-44.4	30.1	-78.3	17.5	0.07	17.9	0.138
fass	-45.6	31.5	-16.3	14.9	0.05	0.47	0.033
mel-9	-8.6	3.0	-409.9	58.8	130.8	197.3	0.006

*Mineral phase: spot number in each sample analyzed. Repeated analyses in the same spot are indicated by ".1." Abbreviations: mel, melilite; alt, alteration; fass, fassaite; and n.d., not determined.

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calculated $^{11}\text{B}/^{10}\text{B} \approx 135$ (30), in disagreement with the CAI ratio.

It is thus unlikely that the CAI 3529-41 could have inherited much of its complement of radioactive Be from the presolar cloud, but it is plausible that the ^{10}Be could have been produced locally within the solar nebula. Possible analogs for the early solar system are provided by YSOs, forming low-mass stars that produce copious x-rays with spectral characteristics similar to solar flares (25). The ubiquitous x-ray signature of YSOs indicates that it is possible that a fraction of the material in the solar nebula went through a period of intense irradiation in the vicinity of the sun (32). It has been proposed that CAIs formed at the inner edge of the solar accretion disk where they are heavily irradiated before being launched to greater heliocentric distance where they may accrete into chondrite parent bodies (5, 12). In YSOs, the flux of energetic protons accompanying flares should be at least 3×10^5 times the present-day solar flux, i.e., $\Phi = 2 \times 10^9 \text{ H cm}^{-2} \text{ s}^{-1}$ at 0.1 astronomical unit (33), and impulsive flares may provide an even higher flux (5). The corresponding irradiation time that yields the ^{10}Be content in the CAI can be calculated to be on the order of decades to 100 years. This duration is also sufficient to produce other short-lived nuclides, ^{41}Ca and ^{53}Mn , at the abundance levels found in meteorites (34), but the canonical CAI abundance of ^{26}Al cannot be reached unless other energetic particles (e.g., ^3He) and special target shielding configurations are considered (5). Alternatively, it may be possible to obtain the correct relative levels of ^{41}Ca , ^{26}Al , and ^{10}Be in an irradiated Ca-Al-depleted silicate dust, such as refractory olivine, which is evaporated after, or during, the irradiation. A mechanism for quantitative distillation of radioisotopes into CAI melts needs to be elaborated before it can be concluded that such a scenario can explain all the important short-lived nuclides in CAIs by local production. Finally, we note that in a local irradiation scenario, the low initial $\delta^{11}\text{B}$ accompanying live ^{10}Be in an early formed CAI can be interpreted as reflecting the progressive production in the solar nebula of ^{11}B -rich B by low-energy irradiation. If this is correct, higher initial $\delta^{11}\text{B}$ values in CAIs should be associated with higher $^{10}\text{Be}/^9\text{Be}$ ratios.

References and Notes

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- Short-lived isotopes identified in meteorites include ^{26}Al , ^{41}Ca , ^{53}Mn ($\tau_{1/2} \sim 3.7 \text{ My}$), ^{107}Pd ($\tau_{1/2} \sim 6.5 \text{ My}$), and ^{129}I ($\tau_{1/2} \sim 15.9 \text{ My}$). The first evidence for in situ decay was the determination by T. Lee, D. Papanastassiou, and G. J. Wasserburg [*Geophys. Res. Lett.* **3**, 109 (1976)] that the degree of excess ^{26}Mg in minerals separated from a CAI from the Allende carbonaceous chondrite varied linearly with the Al/Mg ratio. Lee *et al.* inferred an initial $^{26}\text{Al}/^{27}\text{Al}$ ratio of $\sim 5 \times 10^{-5}$ at the time of CAI formation, which has subsequently been shown to characterize such a large fraction of CAIs examined that it is often considered to be a “canonical” value characteristic of the earliest epoch of solar system formation (35). Recently, a small number of CAIs and refractory hibonite grains from carbonaceous chondrites have been found to contain excess ^{41}K in proportion to their Ca/K ratios, implying that these minerals crystallized with $\sim 10^{-8}$ of their Ca as radioactive ^{41}Ca (3).
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- For example, the short half-life of ^{41}Ca constrains the interval between nucleosynthetic production and the incorporation of radionuclides into CAIs to less than a few hundred thousand years, suggesting that collapse of a molecular cloud fragment to form the solar nebula was triggered by a shock wave associated with the same stellar event (e.g., a supernova explosion) that generated the short-lived isotopes (29). In this scenario, the injection of this late spike of freshly synthesized stellar products would provide a time zero from which a high-resolution chronology of early solar system processes could be deduced on the basis of the decay of the short-lived isotopes. In contrast, if radioisotopes were locally produced, then not only would constraints on collapse time scales be obviated but also differing initial abundances in discrete components of primitive meteorites could result from variable production rather than decay from a canonical value, rendering chronological interpretations invalid.
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- Type B CAIs, which typically occur as millimeter- to centimeter-sized inclusions in CV3 carbonaceous chondrites, contain melilite, Ti-Al-rich pyroxene, anorthite, and Mg-spinel as major minerals. The petrography, mineral chemistry, and Mg isotopic compositions of the samples analyzed here have been described previously by (75) for 3529-30 and 3529-41 and by (36) for TS-34. Briefly, 3529-30 contains millimeter-sized anhedral melilite laths that are in places partially altered to fine-grained anorthite and grossular. The Al-Mg system is moderately disturbed with different anorthite grains exhibiting distinct apparent isochrons, with $^{26}\text{Al}/^{27}\text{Al}$ initial values ranging from 2.7 to 4.6×10^{-5} (75). Inclusion 3529-41 contains a melilite-rich outer mantle, thus making it type B1. Its Al-Mg system exhibits evidence for only minor postcrystallization disturbance: Anorthite shows a good isochron indicating $(^{26}\text{Al}/^{27}\text{Al})_0 = 4.1 \times 10^{-5}$, close to the canonical value, but three analyses of melilite indicate minor additions of radiogenic ^{26}Mg (75). The CAI TS-34, formerly named AL354, is a centimeter-sized coarse-grained type B1 inclusion (36). A single analysis (76) of anorthite in TS-34 indicates that it crystallized with canonical ^{26}Al , but the data are insufficient to conclude whether or not its Al-Mg isotopic system has suffered disturbance.
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- Isotopic compositions and atomic concentrations of Li-Be-B were analyzed in situ within polished, C-coated thin sections with the CAMECA ims 1270 ion microprobe at the CRPG-CNRS, Nancy. Techniques for isotopic measurements were similar to those previously described for the analysis of B isotopes in terrestrial mantle rocks having $<1 \text{ ppm}$ of B (37). The primary difficulties with the measurements of CAIs are the low concentrations of Li-Be-B and contamination of the sample surface by extraneous boron. Our analysis routine was first to remove surficial B contamination by rastering an intense $^{16}\text{O}^-$ ion beam over the area of interest and then to use a focused static ion beam of ~ 10 to 30 nA with a field aperture inserted into an image plane of the secondary ion beam to restrict the analyzed area to the central part of the sputtered crater. Isotope ratio measurements were performed by cycling the magnet through the mass sequence: 5.8, ^6Li , ^7Li , ^9Be , ^{10}B , 10.02708, ^{11}B with integration times typically set to 1, 4, 2, 2, 10, 2, and 3 s, respectively, and the number of cycles adjusted according to count rate. Analysis times ranged from 20 min to 2 hours. The mass stations 5.8 and 10.02708 were counted to monitor the dynamic background during the analysis; the lower mass provides an estimate of the noise of the ion counting system, and the other mass was included specifically to check for additional spectral contributions from possible scattered BeH^+ ions that could appear as $^{10}\text{B}^+$. No such scattered ions were found, and, with a mass resolution of 2000 used to separate hydride molecules as well as triply charged species of Al and Si, the mass spectrum was completely clean of interfering ions. The dynamic background was constant within statistical limits over analysis sessions lasting several days at a level of $\sim 0.03 \text{ s}^{-1}$. Ion intensities were corrected for background and for counting system dead time (negligible correction for the CAI analyses). The maximum contribution of this background correction occurs for the spot of 3529-41 that exhibits the most anomalous B isotope composition with count rates of 0.52 s^{-1} and 1.17 s^{-1} , respectively, for the $^{10}\text{B}^+$ and $^{11}\text{B}^+$ signals. Even in this case, the background amounts to $<10\%$ of the observed anomaly, and the uncertainty in this correction is smaller than the error due to counting statistics. Instrumental mass fractionation (IMF) was corrected by comparison with analyses of the GB4 synthetic silicate glass standard (37). The observed IMF was similar to that previously reported, and possible errors due to matrix effects on IMF are insignificant (37). The corrected Li and B isotope ratios are reported in Table 1 as $\delta^7\text{Li}$ and $\delta^{11}\text{B}$, the deviations relative to the standards $^7\text{Li}/^6\text{Li}_{\text{NBS-LVSEC}} = 12.0192$ and $^{11}\text{B}/^{10}\text{B}_{\text{NBS951}} = 4.04558$, expressed in ‰. After isotope determinations, a new analysis was made in the same spot to obtain the ratios of $^7\text{Li}^+$, $^9\text{Be}^+$, and $^{11}\text{B}^+$ relative to $^{28}\text{Si}^+$ for calculation of elemental concentrations. Relative sensitivity factors were determined by separate measurements of the GB4 standard. Uncertainties on isotope ratios are dominated by counting statistics, but because of potential matrix effect problems, relative and absolute concentrations of Li, Be, and B are probably accurate to only $\sim 10\%$ and $\sim 50\%$, respectively.
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 24. Although Be is concentrated in melilite, large Be/B fractionations are achieved only when the degree of B depletion is also high. In the case of Allende 3529-30, B abundances are not depleted but are instead enriched relative to CI values. One analyzed spot, with a B concentration of ~10 ppm, consists primarily of fine-grained alkali-rich minerals thought to be secondary phases produced during alteration of the original CAI assemblage. We interpret the high B abundances and near-normal $\delta^{11}\text{B}$ values of 3529-30 as reflecting the reintroduction of B into the CAI during the secondary alteration event(s), whether in the nebula or in an asteroidal setting. Recent ion microprobe measurements [K. K. Marhas and J. N. Goswami, *Curr. Sci.* **78**, 78 (2000)] of B in anorthite from an Efremovka CAI show normal $\delta^{11}\text{B}$ values, consistent with the high B concentrations and low Be/B expected for anorthite.
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 34. The X-wind model makes definitive predictions for irradiation of CAI precursors based on a scaling of x-ray luminosity of YSOs to the flux of particles accelerated in solar flares (5). With cross sections for $^{16}\text{O}(p,x)^{10}\text{Be}$ from (13) and assuming an energy spectrum characteristic of impulsive flares that scales

as $E^{-3.5}$, and estimating the ^9Be concentration in the CAI 3529-41 as ~350 ppb (~14 × CI), we calculate [equation 20 of (5)] an initial $^{10}\text{Be}/^9\text{Be}$ of 0.0005, which is within a factor of 2 of the measured value. A deficit of this magnitude is within the systematic uncertainties of these calculations and can be made up by either a slightly flatter proton spectrum or a substantial contribution to ^{10}Be production from He spallation. The same irradiation parameters and cross sections summarized in (9) yield values of $^{41}\text{Ca}/^{40}\text{Ca}$ and $^{53}\text{Mn}/^{55}\text{Mn}$ that are compatible with those observed in CAIs (5).
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Primordial Carbonylated Iron-Sulfur Compounds and the Synthesis of Pyruvate

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Experiments exploring the potential catalytic role of iron sulfide at 250°C and elevated pressures (50, 100, and 200 megapascals) revealed a facile, pressure-enhanced synthesis of organometallic phases formed through the reaction of alkyl thiols and carbon monoxide with iron sulfide. A suite of organometallic compounds were characterized with ultraviolet-visible and Raman spectroscopy. The natural synthesis of such compounds is anticipated in present-day and ancient environments wherever reduced hydrothermal fluids pass through iron sulfide-containing crust. Here, pyruvic acid was synthesized in the presence of such organometallic phases. These compounds could have provided the prebiotic Earth with critical biochemical functionality.

In all extant organisms, transition metal sulfide clusters play a crucial catalytic role in biological energy conversion systems (1). The potential connection between this essential role and the predominance of mineral sulfides in hydrothermal and volcanic vents has led some to speculate that life may have emerged from such environments (2). Such a connection is further supported by the natural history of bacterial lineages (3).

Recently, experiments designed to replicate aspects of the primitive hydrothermal vent solution chemistry have revealed the intrinsic potential for the synthesis of alkyl thiols (4) from reactions involving iron sulfides in the presence of CO. The formation of

acetate (5) has been demonstrated in aqueous solutions containing methyl thiol and CO in the presence of iron and nickel sulfides. Huber and Wächtershäuser (5) proposed that iron and nickel sulfides grossly mimic the functionality of acetyl coenzyme A (CoA) synthase, the iron- and nickel-containing enzyme complex present in chemoautotrophic anaerobic organisms (6).

In the experiments described above, surfaces of transition metal sulfides presumably served to bind both alkyl groups and carbon monoxide, thus promoting carbon reduction as well as carbonyl insertion reactions (7). Both these experiments were performed at relatively low temperatures and pressures. At elevated temperatures and pressures, such as those attained in shallow oceanic crust, transition metal sulfides are likely to react with both CO and alkyl thiols (and/or disulfides) to produce sulfur-containing transition metal car-

bonyls (8). The natural synthesis of such compounds through the interaction of reduced crustal fluids with transition metal sulfides precipitated in Hadean crust could have provided a natural source for carbonylated organometallic species. Here, we describe the results of geochemical experiments that explore the formation of such complexes under conditions of high pressure and temperature.

Our experiments were run in welded gold tube reactors charged with 15.0 mg (170 μmol) of pure iron sulfide (9), 5.0 mg (31 μmol) of alkyl (nonyl) thiol, and 5.0 mg (110 μmol) of formic acid (99.9%). Formic acid was used as a source of reactive C_1 (organic molecules with one C atom); that is, CO and H_2O are formed through the thermal decomposition of formic acid (10) and equilibrated with CO_2 and H_2 through the water-gas shift reaction. Although formic acid was chosen primarily as a source of CO, it has been detected in present-day vent fluids (11). The initial concentrations of thiol and C_1 compounds were chosen to ensure a large excess of substrate per available mineral surface area [~10,000 substrate molecules per surface site (12)]. Multiple experiments were run at elevated pressures (50, 100, and 200 MPa) and held at $250^\circ \pm 0.2^\circ\text{C}$ for 6 hours with the use of a gas pressure apparatus (13). Additional blank experiments in Au (without minerals) were run and analyzed under identical conditions to address the potential catalytic activity of Au; the results revealed only nonyl thiol as the recovered product.

After reaction, each reactor was stored frozen at -87°C until processing and was immersed in liquid N_2 immediately before opening. Quantitative analysis of nonyl-containing organic compounds was performed on triplicate runs obtained at each pressure, with the use of gas chromatography–mass spectrometry (GC-MS) detection, a calibration standard, and standard esterification proce-

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