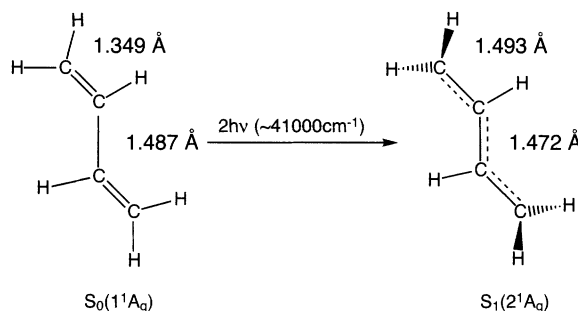


Scheme 2. Geometrical changes in the butadiene molecule induced by the $S_0 \rightarrow S_1$ two-photon electronic transition. The bond distances (23, 24) are expressed in Å.



cis-trans isomerization (23, 24), while experimental (26) and theoretical (27) studies on reactions involving more butadiene molecules are limited. These reactions seem to occur through conical intersections between the energy surfaces of the S_1 (2^1A_g) and the S_0 states (24, 25, 27), explaining the efficient nonradiative decay and the low selectivity (large number of products) of the photo-induced reactions.

The mechanism of the high-pressure polymerization can be pictured as follows. In the S_1 state, the outer C_1 - C_2 and C_3 - C_4 backbone bond lengths increase by $\sim 10\%$ compared with the ground state and become larger than the C_2 - C_3 bond length (28, 29). This structural change is accompanied by a lowering of the torsional barrier such that a nearly free rotation of the terminal $-CH_2$ groups is possible (Scheme 2). The geometry changes, together with the long lifetime of the S_1 state, which allows collisions with the nearest neighbor molecules, favor a development of the reaction along the molecular backbone and, at the same time, prevent the dimerization, which requires an overlapping of π bonding electron densities of nearest neighbor molecules.

The present experiments give clear evidence that laser irradiation plays a fundamental role in the activation of the polymerization that prevails over the competing dimerization process. The obtainment of pure *trans*-polybutadiene is indeed a remarkable result. As a whole, the high-pressure reaction studied in the present report has several interesting features including the high selectivity of the process, the easy switching from one pathway to the other, and the full transformation into the product with the absence of solvents and catalysts, thus fulfilling several of the requirements for a green chemistry process (30).

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at 7.4 eV. The 488-nm Ar^+ line corresponds to a two-photon energy of 5.1 eV ($\sim 41,000\text{ cm}^{-1}$) and is in much better agreement with the results of a resonance Raman investigation that locates the 2^1A_g state at about $44,300\text{ cm}^{-1}$ ($\sim 5.5\text{ eV}$) with a width of 4000 to 5000 cm^{-1} (21). According to this latter estimate and considering the usual redshift of the excited electronic state at high pressure, irradiation in the present experiment corresponds to pumping in the low-frequency edge of the 2^1A_g level. Because in the present experiment the laser light is unambiguously absorbed via a two-photon mechanism, we are able to locate the 2^1A_g state of butadiene well below the calculated values in agreement with the results of resonance Raman spectroscopy (21).

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Chromium Isotopes and the Fate of Hexavalent Chromium in the Environment

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Measurements of chromium (Cr) stable-isotope fractionation in laboratory experiments and natural waters show that lighter isotopes reacted preferentially during Cr(VI) reduction by magnetite and sediments. The $^{53}\text{Cr}/^{52}\text{Cr}$ ratio of the product was 3.4 ± 0.1 per mil less than that of the reactant. $^{53}\text{Cr}/^{52}\text{Cr}$ shifts in water samples indicate the extent of reduction, a critical process that renders toxic Cr(VI) in the environment immobile and less toxic.

Chromium is a common contaminant in surface water and groundwater (1, 2) because it is used widely in electroplating and other

industries and occurs naturally at high concentration in ultramafic rocks. Under oxidizing conditions, Cr is highly soluble and mobile as the Cr(VI) anions chromate (CrO_4^{2-}) and bichromate (HCrO_4^-). Cr(VI) is a suspected carcinogen (3). Under reducing conditions, Cr(VI) may convert to Cr(III), which is insoluble, strongly adsorbed onto solid surfaces (4), and less toxic. Cr(VI) can be removed from solution artificially by in situ reduction (5, 6), or naturally by reductants

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such as aqueous Fe(II), dissolved humic acids, and Fe(II)-bearing minerals (7, 8).

For these reasons, knowledge of reduction rates is essential in many Cr(VI) contamination cases. For example, sufficient rates of natural reduction at a given site allow use of the "monitored natural attenuation" approach, which is much less expensive and disruptive than active remediation. Determining reduction rates can be difficult; multiple rounds of groundwater sampling and analysis over several years has been required in some contaminant plumes. Reduction reactions tend to enrich products in the lighter isotopes because they preferentially react (9), and the residual reactants become progressively enriched in the heavier isotopes as reduction proceeds (10–12). Here we show that Cr stable isotopes can be used to estimate the extent of reduction, which in turn can be used to estimate long-term reduction rates.

Cr has four stable isotopes of masses 50 (4.35%), 52 (83.8%), 53 (9.50%), and 54 (2.37%) (13). We developed a double-isotope spike method for measuring mass-dependent fractionation of Cr isotopes (i.e., variations in the relative abundances of light and heavy isotopes) (14). We measured Cr isotope fractionation during reduction of Cr(VI) by slurries of magnetite and two sediment samples (15). Because magnetite is a likely reducing agent in some aquifer sediments (16), the magnetite experiment provides a simple analog for a natural aquifer. The sediment slurries were microbially rich and chemically complex, and were collected from an intertidal mud flat in the northern reach of the San Francisco Estuary and from a pond in Urbana, Illinois. The water in the estuary is about 50% seawater, and the sediment was silt with a total organic carbon (TOC) content of 0.92%. The Urbana pond is freshwater runoff, and its sediment was clayey silt with a TOC of 0.29%.

In the magnetite suspensions, a sharp initial decrease in Cr(VI) was followed by a slower, linear decrease (Fig. 1). In the sediment slurry experiments, Cr(VI) concentrations followed roughly a first-order trend (Fig. 1). As expected at pH 6 to 7, sorption of Cr(VI) was negligible. We confirmed the

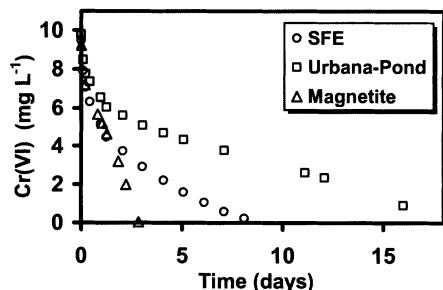


Fig. 1. Cr(VI) concentration versus time in the experiments. SFE, San Francisco Estuary.

lack of reversible sorption by adding competing anions like sulfate and phosphate to desorb any adsorbed Cr(VI); no effects were observed. As reduction proceeded and the Cr(VI) concentrations decreased, $\delta^{53}\text{Cr}$ values of the remaining unreduced Cr(VI) increased, indicating preferential reduction of the lighter isotopes (Fig. 2). To calculate the size of this kinetic isotope effect, we used a Rayleigh fractionation model. The instantaneous isotope fractionation factor, α , is defined by

$$\alpha = R_{\text{prod}}/R_{\text{react}} \quad (1)$$

where R_{prod} and R_{react} are the $^{53}\text{Cr}/^{52}\text{Cr}$ ratios of the Cr reduced at an instant in time and in the reactant pool, respectively. The α values were calculated using the relation

$$\delta^{53}\text{Cr} = [(\delta^{53}\text{Cr}_{\text{ini}} + 10^3)f^{(\alpha-1)}] - 10^3 \quad (2)$$

where $\delta^{53}\text{Cr}$ and $\delta^{53}\text{Cr}_{\text{ini}}$ (14) refer to the unreacted Cr(VI) pool at the time of sampling and at the start of the experiment, respectively, and f is the fraction of Cr(VI) remaining. In all cases, models fit the data within the uncertainties (Fig. 2 and Table 1). Autoclaved control duplicates of the two sediment experiments reduced Cr(VI) as quickly as the unautoclaved experiments did, hence the reduction was abiotic.

These experiments show that reduction of Cr(VI) results in Cr stable-isotope fractionation. The similarity of the α values determined for the three contrasting experiments suggests that the reduction mechanisms are similar, despite the differences in the reducing agents. Given that the reactions were abiotic, the similarity of the isotope ratio shifts likely reflects the kinetic isotope effect accompanying the breakage of Cr-O bonds of the Cr(VI) oxyanions. If so, these results should be applicable to aquifers where abiotic reduction dominates.

We obtained groundwater samples from sites in Putnam, Connecticut, and Berkeley, California (17). Both are contaminated by Cr plating wastes. At the California site, ground-

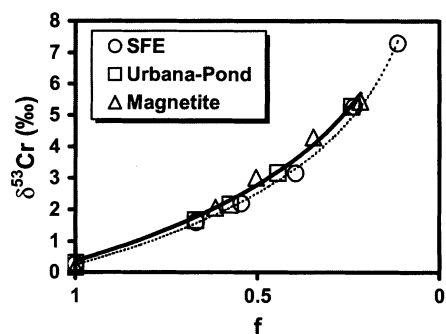


Fig. 2. $\delta^{53}\text{Cr}$ of unreduced dissolved Cr(VI) versus f , the fraction of Cr(VI) remaining. Dark line, $\alpha = 0.9965$ best-fit curve for Urbana pond and magnetite experiments. Dotted line, $\alpha = 0.9967$ best-fit curve for the San Francisco Estuary experiment.

water flows through natural alluvium and artificial fill. On the basis of several years of data, previous workers concluded that Cr(VI) has been partially removed from solution, probably by reduction (18). At the Connecticut site, groundwater flows through glacial deposits that likely contain magnetite and other Fe(II)-bearing minerals.

To estimate the initial isotopic compositions of the contaminants, we measured $\delta^{53}\text{Cr}$ in samples of three plating baths in active use, two at the Connecticut site and a third from another location with a different plating process (Table 2). We also analyzed the chromic acid supply used to make up plating baths at the Connecticut site, two laboratory Cr reagents, and three basaltic rock standards (19) representing diverse geologic environments (Table 2). The rock analyses provided information about the bulk $\delta^{53}\text{Cr}$ of Earth. All of these samples yielded $\delta^{53}\text{Cr}$ values close to zero. Cr ores are of igneous origin; because little isotopic fractionation is expected at high temperatures, these ores should (and apparently do) inherit $\delta^{53}\text{Cr}$ values from Earth's mantle. We expect that Cr isotopes are not fractionated during purification (20), and thus most or all supplies of industrial Cr should have $\delta^{53}\text{Cr}$ values close to 0‰, like the samples measured here.

The plating bath samples also had $\delta^{53}\text{Cr}$ values close to 0‰, with a mean of 0.34‰. This is somewhat surprising, because Cr(VI) reduction is essential to the plating process and large amounts of Cr are removed from the plating baths by this reaction. Roughly one-tenth of the Cr(VI) is consumed in a typical week, after which the lost Cr(VI) is replenished. This cycle has been repeated for more than 5 years in the two Connecticut baths. A simple model of this process reveals that an isotopic fractionation factor of 0.9997 for Cr(VI) removed by the plating reaction would result in a steady-state value of +0.3‰ for the plating bath relative to the Cr(VI) supply after about 20 cycles.

In light of these observations, we suggest that Cr released as plating waste generally has an initial $\delta^{53}\text{Cr}$ value slightly greater than zero. If so, detection of Cr(VI) reduction in groundwater systems would be relatively simple, as the initial $\delta^{53}\text{Cr}$ value would be known and groundwater values greater than that would directly indicate the extent of reduction. If, on the other hand, plating wastes have variable $\delta^{53}\text{Cr}$ values, then it

Table 1. Isotopic fractionation in Cr(VI) reduction experiments.

Reducing agent	α
Magnetite	0.9965
Estuarine sediment	0.9967
Pond sediment	0.9965

may be possible to distinguish different contamination sources via their $\delta^{53}\text{Cr}$ values.

Our measured groundwater $\delta^{53}\text{Cr}$ values (Table 2) ranged from 1.1 to 5.8‰ in the samples from the California site, and from 1.3 to 4.0‰ in the samples from the Connecticut site. All of the groundwater Cr(VI) analyses show enrichment in the heavy isotope relative to the plating baths. Apparently, Cr(VI) reduction has preferentially removed lighter isotopes from the groundwater. The variation in $\delta^{53}\text{Cr}$ values at each site suggests that reduction of Cr(VI) is occurring and has progressed to different degrees in different parts of the contaminant plumes. The highest $\delta^{53}\text{Cr}$ values are found in the samples with lowest Cr(VI) concentration at both sites. This result is expected because the fringe areas of the contaminant plumes likely have greater degrees of reduction than the plume cores, where Cr concentrations are high and the reducing power of the aquifer materials has been depleted.

Stable Cr isotope ratios can thus serve as indicators of the extent of Cr(VI) reduction in groundwater. For example, if we assume an α value of 0.9966 and a value of 0.34‰ (the mean of the plating bath analyses) for the initial $\delta^{53}\text{Cr}$ of the contaminant Cr, we can use Eq. 1 to determine the extent of reduction for two of the Connecticut groundwater samples, MW-9 and MW-12; for these samples, 31% and 68% of the Cr(VI) initially present in the wells was reduced, respectively.

Cr(VI) reduction by bacteria or reducing agents other than those studied here could induce greater or lesser isotopic fractionation than we observed. Processes other than reduction, such as sorption, precipitation, and uptake by plants and algae, can remove Cr from solution (1, 21–23). If these processes and/or Cr(III) oxidation induce isotopic fractionation, this

could complicate the interpretation of $\delta^{53}\text{Cr}$ measurements. However, as with S and Se isotopes (12), we expect that the dominant cause of Cr isotope fractionation is oxyanion reduction. Cr isotope studies may also be useful in assessing redox conditions in modern or ancient oceans.

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(‰) = $[(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sam}} - (^{53}\text{Cr}/^{52}\text{Cr})_{\text{std}}]/(^{53}\text{Cr}/^{52}\text{Cr})_{\text{std}} \times 1000$, where sam and std refer to sample and National Institute of Standards and Technology Standard Reference Material 979, respectively. External measurement precision is $\pm 0.2\text{‰}$.

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Mammalian Dispersal at the Paleocene/Eocene Boundary

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A profound faunal reorganization occurred near the Paleocene/Eocene boundary, when several groups of mammals abruptly appeared on the Holarctic continents. To test the hypothesis that this event featured the dispersal of groups from Asia to North America and Europe, we used isotope stratigraphy, magnetostratigraphy, and quantitative biochronology to constrain the relative age of important Asian faunas. The extinct family Hyaenodontidae appeared in Asia before it did so in North America, and the modern orders Primates, Artiodactyla, and Perissodactyla first appeared in Asia at or before the Paleocene/Eocene boundary. These results are consistent with Asia being a center for early mammalian origination.

Most modern groups of mammals first appeared on the Holarctic continents (Asia, Europe, and North America) in the early Paleogene (1–6). Phylogenetic hypotheses point to Asia as the center of origin for many groups (4), but intercontinental correlation of faunas

is poorly constrained. The Paleocene/Eocene (P/E) boundary is marked by a short-lived [$\sim 80,000$ -year (7, 8)] decrease in the $\delta^{13}\text{C}$ of marine (9–11) and terrestrial carbon (8, 12, 13) occurring within the lower third of magnetic polarity chron C24r (7, 9). The first known

Table 2. Cr isotope ratio determinations.

Sample	[Cr(VI)] (mg/liter)	$\delta^{53}\text{Cr}$ (‰)
Reagent Cr, rocks		
K ₂ Cr ₂ O ₇ reagent	—	0.35
Cr(NO ₃) ₃ reagent	—	0.32
BIR basalt (Iceland)	—	−0.04
BHVO basalt (Kilauea)	—	0.05
JB basalt (Japan)	—	−0.04
Plating bath	$\sim 10^5$	0.37
Connecticut site		
Plating bath 1	$\sim 10^5$	0.36
Plating bath 2	$\sim 10^5$	0.29
CrO ₃ supply	—	−0.07
MW-8 groundwater	4.5	2.23
MW-9 groundwater	8.61	1.28
MW-11s groundwater	16.1	1.93
MW-11 groundwater	0.63	3.62
MW-12 groundwater	1.63	3.96
California site		
MW-3 groundwater	0.98	1.08
MW-10 groundwater	0.13	5.79
MW-12 groundwater	3.1	3.39