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Chromium, chromium isotopes and selected trace elements, western Mojave Desert, USA

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Abstract

Chromium(VI) concentrations in excess of the California Maximum Contaminant Level (MCL) of 50 μg/L occur naturally in alkaline, oxic ground-water in alluvial aquifers in the western Mojave Desert, southern California. The highest concentrations were measured in aquifers eroded from mafic rock, but Cr(VI) as high as 27 μg/L was measured in aquifers eroded from granitic rock. Chromium(VI) concentrations did not exceed 5 μg/L at pH < 7.5 regardless of geology. δ^{53}Cr values in native ground-water ranged from 0.7 to 5.1‰ and values were fractionated relative to the average δ^{53}Cr composition of 0‰ in the earth's crust. Positive δ^{53}Cr values of 1.2 and 2.3‰ were measured in ground-water recharge areas having low Cr concentrations, consistent with the addition of Cr(VI) that was fractionated on mineral surfaces prior to entering solution. δ^{53}Cr values, although variable, did not consistently increase or decrease with increasing Cr concentrations as ground-water flowed down gradient through more oxic portions of the aquifer. However, increasing δ^{53}Cr values were observed as dissolved O_2 concentrations decreased, and Cr(VI) was reduced to Cr(III), and subsequently removed from solution. As a result, the highest δ^{53}Cr values were measured in water from deep wells, and wells in discharge areas near dry lakes at the downgradient end of long flow paths through alluvial aquifers. δ^{53}Cr values at an industrial site overlying mafic alluvium having high natural background Cr(VI) concentrations ranged from −0.1 to 3.2‰. Near zero δ^{53}Cr values at the site were the result of anthropogenic Cr. However, mixing with native ground-water and fractionation of Cr within the plume increased δ^{53}Cr values at the site. Although δ^{53}Cr was not necessarily diagnostic of anthropogenic Cr, it was possible to identify the extent of anthropogenic Cr at the site on the basis of the δ^{53}Cr values in conjunction with major-ion data, and the δ^{18}O and δD composition of water from wells.
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1. Introduction

Chromium, the 17th most abundant element in the earth's crust (Hem, 1970), occurs naturally in water in either the Cr(III) or Cr(VI), oxidation state. Chromium(III) is an essential micronutrient for

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humans. Chromium (VI) associated with atmospheric aerosols is a toxin and a carcinogen if inhaled (ATSDR, 2000; Daugherty, 1992), although the toxicity and carcinogenicity of Cr(VI) ingested in water is uncertain.

Chromium occurs naturally in water from alluvial aquifers in the western part of the Mojave Desert (Ball and Izbicki, 2004), elsewhere in the arid southwestern USA (Robertson, 1975, 1991), and in other parts of the USA and the world (Gonzalez et al., 2005; Gray, 2004). In alluvial aquifers such as those underlying the western Mojave Desert (Fig. 1) where native ground-water is oxic and has pH values commonly exceeding 8 and occasionally exceeding 9, oxidized Cr(VI) predominates (Ball and Izbicki, 2004). Where geochemical conditions are favorable, and Cr concentrations in source rock are high, naturally-occurring Cr concentrations in ground-water may exceed the California Maximum Concentration Limit of 50 μg/L (Ball and Izbicki, 2004). In the past, regulatory concern has focused on anthropogenic sources of Cr. However, increasing population growth in arid areas dependent on ground-water having high natural Cr(VI) concentrations has increased concern about naturally-occurring concentrations of Cr (Gonzalez et al., 2005).

In areas having high natural background Cr concentrations, such as the Sheep Creek fan of the western Mojave Desert, it may be difficult to distinguish natural Cr from that associated with industrial or other discharges. In these areas, Cr isotopes may help distinguish Cr originating from natural sources to that originating from anthropogenic sources.

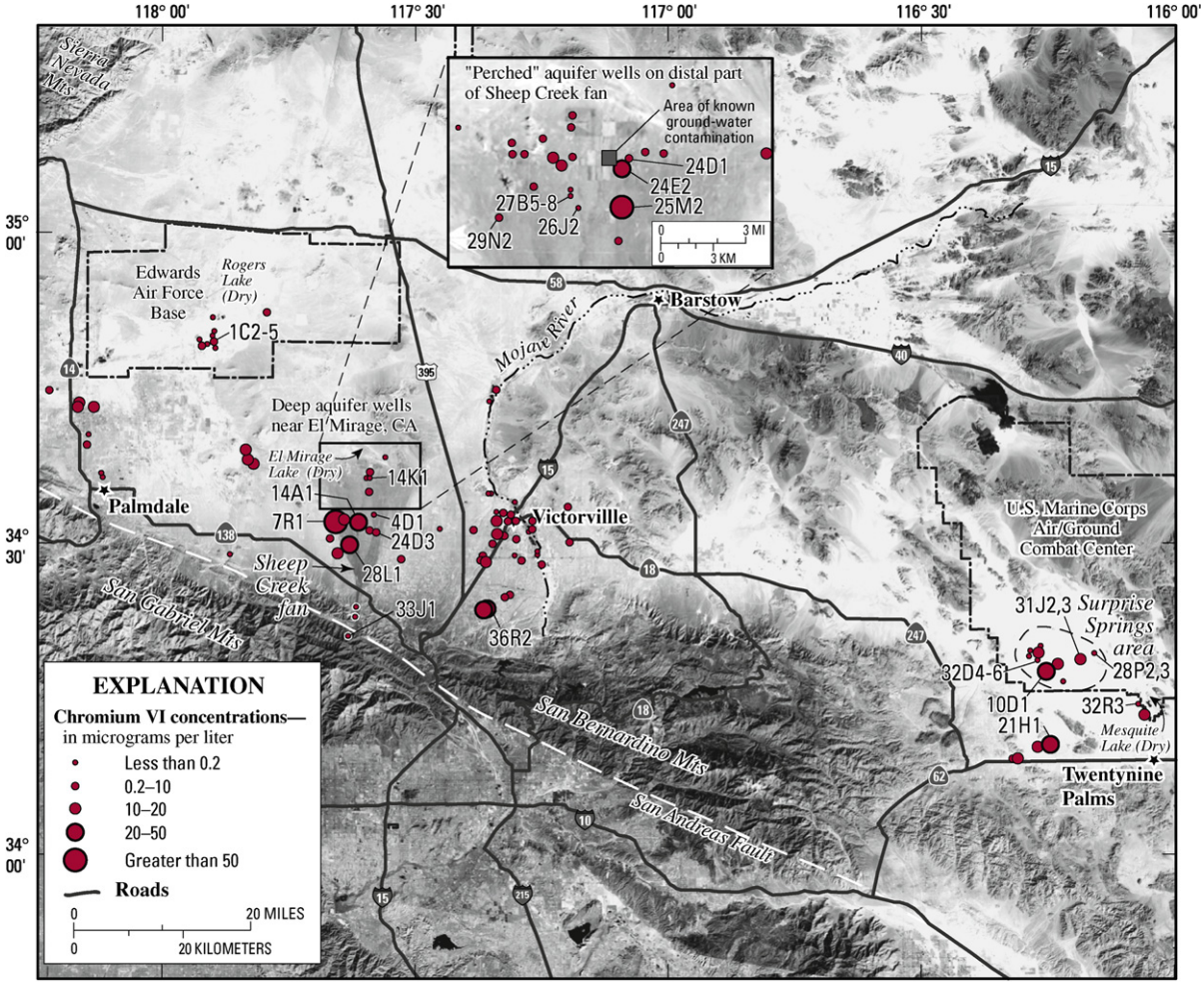

Fig. 1. Study area location.

1.1. Abundance of chromium, chromium isotopes and selected trace elements

The average concentration of Cr in the earth's crust is about 100 μg/g (Nriagu, 1988; Reimann and Caritat, 1998). Chromium concentrations are higher in basaltic and ultramafic rocks, which have average concentrations of about 200 and 2400 μg/g, respectively (Nriagu, 1988; Reimann and Caritat, 1998), than in granitic rocks, which have an average concentration of 10 μg/g (Reimann and Caritat, 1998). The most common Cr-containing mineral is chromite ($FeCr_2O_4$). Chromium is commonly substituted within minerals such as amphiboles, garnets, micas, pyroxenes, and spinels (Reimann and Caritat, 1998). Chromium in chromite and that substituted within most minerals occurs in the +3 oxidation state (Nriagu, 1988).

The aqueous environmental geochemistry of Cr is complex because it has two oxidation states, Cr(III), a cation (Cr^{+3}), and Cr(VI), an oxyanion (CrO_4^{-2} or $HCrO_4^-$), having different chemical behaviors (Rai and Zachara, 1984). Chromium(III) is the predominant form in most minerals and in water under reducing to moderately oxidizing conditions (Rai and Zachara, 1984). In most natural systems, Cr(III) weathered from rock does not enter solution because it is strongly sorbed on mineral surfaces (Rai and Zachara, 1984). Some of the sorbed Cr(III) may be incorporated into the structure of minerals, such as chromite ($FeCr_2O_4$), and sequestered from exchange reactions with the aqueous phase. Oxidation of Cr(III) to Cr(VI) sorbed on mineral surfaces occurs in the presence of Mn oxides (Schroeder and Lee, 1975; Guha et al., 2000). Although oxidation is inhibited in laboratory experiments by the formation of $Cr(OH)_3$ (Fendorf et al., 1992), field studies suggest that oxidation of Cr(III) to Cr(VI) occurs at the longer times scales available in natural settings (Bartlett and James, 1979). Although Cr(VI) is strongly sorbed by Fe oxides at acidic and near neutral pH, it is not strongly sorbed at higher pH or at high ionic strength. Under these conditions, Cr(VI) is available for exchange with the aqueous phase and is the predominant form of Cr in water under oxidizing conditions at high pH. Reduction of Cr(VI) to Cr(III) occurs in the presence of organic material and other reducing agents (Rai and Zachara, 1984). The reduced Cr is rapidly sorbed and removed from solution (Mayer and Schick, 1981; Rai and Zachara, 1984; Charlet and Manceau, 1992).

There are four naturally-occurring isotopes of Cr, having masses of 50, 52, 53 and 54 (White and Cameron, 1948; Audi and Wapstra, 1993; Coplen et al., 2002). The two most abundant isotopes, ^{52}Cr and ^{53}Cr, have abundances of 83.8 and 9.5%, respectively (White and Cameron, 1948; Shields et al., 1966; Rosman and Taylor, 1998; National Nuclear Data Center, 2004). Small natural variations in the ratio of ^{53}Cr to ^{52}Cr can be used to identify Cr from anthropogenic sources or identify chemical processes involving Cr (Ball, 1996; Ball and Bassett, 2000; Ellis et al., 2002, 2004).

Chromium isotopes fractionate during the reduction of Cr(VI) to Cr(III) as the lighter isotope is preferentially reduced, enriching the heavier isotope in the remaining Cr(VI) (Ellis et al., 2002). This reaction may occur on the surfaces of mineral grains or in solution. Weathering of Cr from primary minerals, oxidation of Cr(III) to Cr(VI), and speciation of Cr(VI) between $HCrO_4^-$ and CrO_4^{-2} have not been shown to fractionate Cr in natural settings although limited fractionation may occur as a result of sorption effects, especially near the margins of contaminant plumes (Ellis et al., 2004).

Comparison and contrast of Cr concentrations in different geologic settings with concentrations of other trace elements, such as As, V and U that are mobilized through similar processes may facilitate better understanding of the source, occurrence, and mobility of Cr. These elements also are of public health concern when present in oxic, high pH ground-water at concentrations that exceed their respective Maximum Contaminant Levels (MCL).

Arsenic is less abundant than Cr, having an average concentration in the earth's crust of about 1.8 μg/g, and an average concentration in granitic rock of about 3 μg/g (Reimann and Caritat, 1998). The U.S. Environmental Protection Agency MCL for As was reduced from 50 to 10 μg/L in January, 1996. Naturally-occurring As concentrations in water from wells in the western Mojave Desert commonly exceed the new As MCL (Christensen and Fields-Garland, 2001). Vanadium is slightly more abundant than Cr, having an average concentration in the earth's crust of about 120 μg/g. Vanadium is more abundant in basalts than in either ultramafic or granitic rock (Reimann and Caritat, 1998). Uranium is slightly greater in abundance than As having an average concentration in the earth's crust of about 2.6 μg/g, and a slightly higher average concentration in granitic rock of 4 μg/g (Reimann and Caritat, 1998). Like Cr, As, V and U have complex

aqueous geochemistry, with cationic and oxyanion forms that vary in solubility as a function of pH and redox conditions (Rai and Zachara, 1984; Stumm and Morgan, 1996).

1.2. Purpose and scope

The purpose of this study was to evaluate the geologic, hydrologic and geochemical processes that control natural Cr concentrations and Cr isotopic compositions in ground-water.

The scope of this study included comparison and contrast of the geologic abundance of Cr and its isotopic composition in rock, alluvium and ground-water from two areas in the western Mojave Desert: the Sheep Creek fan west of Victorville and the Surprise Spring area NW of Twenty-nine Palms. Aquifers in the Sheep Creek area were eroded largely from metamorphic rocks in the San Gabriel Mountains and aquifer deposits in the Surprise Spring area were eroded largely from granitic rocks in the San Bernardino Mountains. Concentrations of Cr in alluvium and ground-water also were compared and contrasted with concentrations of other trace elements, including As and to a lesser extent V and U, to illustrate how differences in geologic abundance and chemical properties of these elements combine with hydrology and geochemistry to control trace-element concentrations in ground-water. Chromium isotopic data were used to evaluate geochemical processes that control Cr concentrations in natural waters, and to evaluate the extent of anthropogenic Cr at a site having high natural background concentrations.

2. Geohydrochemical setting

The study area is the western part of the Mojave Desert NE of Los Angeles (Fig. 1). Temperatures in the area exceed 45 °C in the summer and fall below 0 °C in the winter. Precipitation in much of the area is less than 150 mm/a, although the higher altitudes of the San Gabriel and San Bernardino Mountains may receive more than 1000 mm of precipitation in some years, much of it falling as snow during the winter. Except for small streams that drain the higher altitudes in the mountains and for short reaches of the Mojave River where ground-water discharge at land surface maintains streamflow, there are no perennial streams in the area and water supplies are derived almost entirely as ground-water pumped from alluvial aquifers.

In general, recharge to alluvial aquifers in the western Mojave Desert is small relative to the volume of water in storage, and ground-water movement from recharge areas near the mountain fronts to discharge areas is slow. Ground-water in many areas of the Mojave Desert was recharged thousands of years ago (Izbicki et al., 1995; Izbicki and Michel, 2004; Kulongoski et al., 2003, 2005), and the contact time between water and alluvial material is long. Water from deep wells at the down-gradient end of long flow paths through these aquifers may have been recharged more than 20 ka ago (Izbicki et al., 1995; Izbicki and Michel, 2004; Kulongoski et al., 2003, 2005). With the exception of deposits near dry lakes or other wetland areas, most alluvial deposits in the western Mojave Desert contain only small amounts of organic C and are relatively non reactive. Even ground-water recharged many thousands of years BP commonly contains measurable concentrations of dissolved O_2. In aquifers underlying the western Mojave Desert one of the most important reactions between ground-water and alluvium is the slow weathering of primary silicate minerals (Izbicki et al., 1995; Izbicki and Michel, 2004). This weathering consumes large amounts of H^+ and increases the pH of the ground-water. As the pH of ground-water increases along ground-water flow paths, trace elements sorbed on Fe and Mn oxide coatings on mineral grains may exchange with other oxyanions and enter solution (Rai and Zachara, 1984).

Two areas within the western part of the Mojave Desert, the Sheep Creek fan and the Surprise Springs area (Fig. 1), were used to compare and contrast Cr, Cr isotopes, and selected trace-element concentrations in alluvial aquifers from different geologic and geochemical settings.

2.1. Sheep Creek fan

The Sheep Creek fan, west of Victorville (Fig. 1), consists of alluvial deposits eroded from the San Gabriel Mountains. Bedrock in its source area and the alluvial deposits that compose the Sheep Creek fan include both the gray schist and the greenschist facies of the Pelona Schist (Hershey, 1902; Oakeshott, 1958). The source of the distinctive gray color of the gray schist results from fine-grained graphite disseminated in the feldspar of the rock. The color of the greenschist results from chlorite and amphibole minerals (Ehlig, 1958). The Pelona Schist in the headwaters of Sheep Creek has been

extensively deformed, folded, overturned, and metamorphosed. The chemical composition and mineral assemblages of the schist reflect the sedimentary origin of the rock. The degree of metamorphism increases progressively upward (Ehlig, 1968) and greenschist (interlayered with mafic metavolcanic rock composed mostly of feldspar, chlorite, epidote, amphibole and biotite minerals) predominates near the uppermost exposures of the Pelona Schist (Ehlig, 1958). Included within the upper part of the Pelona Schist are mantle-derived, metamorphosed knots of mafic and ultramafic rocks, largely consisting of actinolite (Douglas Morton, U.S. Geological Survey, personal communication, 2004).

The alluvial deposits that compose the Sheep Creek fan are a distinct gray because they contain abundant material eroded from the Pelona Schist. The Pelona Schist has been transported to the west by movement along the San Andreas Fault (Meisling and Weldon, 1989). The distinctive gray sediments eroded from the Pelona Schist are also present at depth in older alluvial deposits of the Victorville fan to the east of the Sheep Creek fan (Meisling and Weldon, 1989; Izbicki et al., 2000).

Alluvial deposits near the mountain front within the apex of the Sheep Creek fan are composed of cobbles in a fine-grained, silty matrix (Izbicki et al., 2000). The deposits become increasingly finer grained with distance from the mountain front toward the distal part of the fan near El Mirage Lake (dry). The alluvial deposits within the distal part of the fan are divided into upper and lower aquifers, known locally as the "perched" and deep aquifers (Smith, 2003). Ground-water in most areas underlying the Sheep Creek fan is unconfined, although the fine-grained deposits near El Mirage Lake (dry) confine ground-water in the underlying deep aquifer. Test-drilling data collected as part of this study show that the deep aquifer in the El Mirage area is composed of alluvium eroded from granitic rock rather than from the Pelona Schist.

Streamflow along Sheep Creek is about 3×10^6 m^3/a (Lines, 1996), and ground-water recharge from infiltration of streamflow is small compared to the volume of water in storage (Stamos et al., 2001; Izbicki et al., 2004). Under present-day climatic conditions, areal recharge does not occur through the unsaturated zone underlying the Sheep Creek fan, although focused recharge occurs along the stream channel near the mountain front (Izbicki et al., 2002). Under predevelopment conditions ground-water flowed from recharge areas near Sheep Creek in the San Gabriel Mountains to discharge areas near El Mirage Lake (dry) and the Mojave River to the east. Ground-water ages, estimated from ^{14}C activities, range from recent (<50 a BP) within the alluvium-filled channel of Sheep Creek in the San Gabriel Mountains to more than 15 ka BP in deeper aquifers farther downgradient from the mountain front (Izbicki et al., 1995; Izbicki and Michel, 2004; Kulongoski et al., 2003). Ground-water levels have dropped in recent years as a result of pumping (Smith, 2003), and the perched aquifer near el Mirage receives small amounts of recharge from infiltration of irrigation-return water.

2.2. Surprise Spring area

The Surprise Springs basin, near Twenty-nine Palms (Fig. 1), consists of alluvial deposits eroded primarily from granitic rocks in the San Bernardino Mountains, but deeper deposits also contain material eroded from metamorphic and volcanic rocks in the local mountains that surround and underlie the granitic alluvium. The metamorphic rocks are different in composition from those in the Sheep Creek area and do not contain minerals high in Cr.

The alluvial deposits within the Surprise Spring basin are bounded by faults to the north, south and east. The deposits are divided into upper and middle aquifers composed primarily of granitic alluvium, and a lower aquifer composed primarily of alluvium eroded from the local mountains. For the purposes of this paper, data from the adjacent ground-water basins to the east was included in the Surprise Spring area. Granitic alluvium from the San Bernardino Mountains is thin and generally above the water table in the Surprise Springs area and saturated alluvium in this area is primarily eroded from the local mountains.

Ground-water recharge occurs from infiltration of streamflow from Pipes Wash in the northwestern part of the Surprise Spring basin (Izbicki, 2004) and is about 0.7×10^6 m/a (Londquist and Martin, 1991). Under natural conditions, ground-water in the basin flowed to the SE toward the discharge area at Surprise Spring (Londquist and Martin, 1991). Faults near Surprise Spring are a barrier to ground-water flow and are responsible for the discharge of ground-water at land surface. Under natural conditions, discharge from Surprise Spring recharged the downgradient basin. However,

analysis of ^{18}O and ^{2}H data (Izbicki, 2004) shows that ground-water farther to the east was recharged from local sources that are not active under present-day climatic conditions.

Despite lower recharge rates, ground-water in the upper aquifer is generally younger than ground-water in the Sheep Creek area and ranges from recent to less than 10 ka BP. This is largely because faults to the north and south of the basin restrict the flow of ground-water in those directions. Ground-water in the lower aquifer system and to the east generally is older than the upper aquifer, and ground-water ages may exceed 10 ka BP (Izbicki and Michel, 2004; Kulongoski et al., 2005). Water levels in the upper aquifer in the Surprise Spring basin have declined as a result of pumping for supply at the Marine Corps Air Ground Combat Center (MCAGCC) at Twenty-nine Palms and ground-water no longer discharges at land surface near Surprise Spring. Ground-water is not pumped for supply from the lower aquifer or from the adjacent basin to the east.

3. Methods

3.1. Analysis of rock and alluvium

Samples of rock from outcrops and core materials and cuttings collected from wells drilled as part of this and other studies were analyzed to determine their mineralogic and trace-element compositions. The samples were sieved and then sorted by density in bromoform having a specific gravity of 2.8, using procedures described by Peacock and Taylor (1990) and Taylor (1990). Minerals containing Cr and other selected trace elements were presumed to be associated with the denser minerals that sank in the bromoform. The dense minerals were then sorted magnetically into highly magnetic (C1), weakly magnetic (C2), and nonmagnetic (C3) fractions. Minerals in the nonmagnetic fraction were identified optically, and then digested and analyzed for trace elements by atomic absorption. Trace-element concentrations of selected samples also were determined using Energy-Dispersive X-Ray Fluorescence (EDXRF) (Criss and Birks, 1968; Currie, 1968).

Selected trace elements were extracted sequentially from operationally-defined fractions on mineral grains in 10 g of oven-dried core, cutting, or alluvial material using a method modified from Chao and Sanzolone (1989). Using this approach, a 0.25 M KCl solution was used to extract trace elements in the water-soluble fraction, a 0.1 M KH_3PO_4 solution to extract trace elements associated with organic material, and a 4 M HCl solution to dissolve Fe, and Mn oxides and associated trace elements on mineral surfaces. After each extraction the solid material was separated from the supernate by centrifugation. The supernate was filtered through 0.45 mm pore-sized filters, preserved with HNO_3, and analyzed for As, Cr, V, U, Fe and Mn. More vigorous extractions used by Chao and Sanzolone (1989) to dissolve sulfides, and silicate minerals were not done.

3.2. Analysis of Cr(VI) and Cr(III), and As(V) and As(III) in water from wells

Samples for analysis of oxidized and reduced forms of Cr and As are difficult to preserve because they are unstable and may change after sample collection. The USEPA requires that samples intended for the analysis of Cr(VI) be preserved at pH > 9.0 and analyzed within 24 h of collection (Arar et al., 1991; Arar and Pfaff, 1991).

Sample preservation methods specified by the USEPA are often impractical at remote sites far from analytical facilities—such as the sites selected for this study. Therefore, samples collected as part of this study were speciated in the field using a technique developed by Ball and McCleskey (2003a,b). The method has a detection limit for Cr (VI) of 0.05 μg/L and a 2σ precision of ±0.21 μg/L (Ball and McCleskey, 2003a,b; Ball and Izbicki, 2004). To use this method, a 0.45-μm pore-size filtered water sample is passed through strong-acid cation-exchange resin. Chromium(III) is retained on the resin, and Cr(VI) passes through the resin. The sample passing through the resin and containing dissolved Cr(VI) was collected, preserved using HNO_3, and analyzed later in the USGS research laboratory in Boulder Colorado using graphite furnace atomic absorption spectrometry (GFAAS). The concentration of Cr(III) was calculated as the difference between the concentration of Cr(VI) in the sample that passed through the resin and the concentration of total Cr measured from a 0.45 μm pore-size filtered sample of water that was not passed through the exchange resin. Because Cr (III) is calculated as a residual the 2σ precision of Cr (III) measurements is likely to be greater than that of Cr (VI) measurements and could be as large as 0.42 μg/L.

To ensure the accuracy of the field speciation, samples collected in May 2001 were analyzed in a mobile field laboratory within hours of collection using a direct colorimetric method (Hach Company, 1992) modified for increased sensitivity by using a laboratory spectrophotometer (Ball and McCleskey, 2003a,b). In addition, samples collected in June 2002 also were analyzed in a mobile field laboratory using the modified direct colorimetric method and the U.S. Environmental Protection Agency method 218.6. The Cr(VI) concentrations measured using the field speciation procedure were similar to concentrations measured in the field using the modified direct colorimetric and USEPA method 218.6. Comparison of the data using least-squares regression analysis produced a line having an intercept and slope not statistically different from 0 and 1, respectively, and an R^2 of 0.9992. (Ball and McCleskey, 2003a,b; Ball and Izbicki, 2004).

In selected samples, total dissolved As and dissolved As(III), were preserved using techniques described by McCleskey et al. (2004). These samples were analyzed in the laboratory using atomic absorption spectrometry with hydride generation (McCleskey et al., 2003). The As(V) concentration was calculated by subtracting the dissolved As(III) concentration from the total dissolved As.

3.3. Analysis of chromium isotopes in water from wells

Chromium was separated from other elements dissolved in water prior to isotopic analysis using a sequential ion-exchange procedure (Ellis et al., 2002) modified from an earlier procedure (Ball, 1996; Ball and Bassett, 2000). This procedure uses anion-exchange to separate Cr(VI), an oxyanion, from interfering cations; and uses cation-exchange to separate Cr(III), a cation, from interfering anions, such as SO_4^{2-}. The sample was passed through an anion-exchange resin (Bio-Rad AG1X8, 100–200 mesh) followed by 15 mL of 0.1 N HCl. The Cr(VI) retained on the anion-exchange resin at pH $\geqslant$ 4 was reduced to Cr(III) and eluted from the resin using 2 N HNO_3. The reduced Cr(III) in the eluted sample was then passed through a strongly-acidic cation-exchange resin (Bio-Rad AG50WX8, 100–200 mesh) at pH $\geqslant$ 1.3. Retained Cr was eluted with 5 N HNO_3. Subsequent processing of the separated sample using H_2O_2 eliminated residual organic material. The sample was subsequently dried and applied to a solid source filament for isotopic analysis of $^{53}Cr/^{52}Cr$ ratios using thermal-ionization mass spectrometry (TIMS). A double spike technique was used to correct for measurement bias introduced by mass-dependent isotope fractionation (Johnson et al., 1999; Ellis et al., 2002; Johnson and Bullen, 2004).

The $^{53}Cr/^{52}Cr$ ratios for National Institute of Standards and Technology Standard Reference Material 979 were measured using the silica gel–boric acid technique with a filament-to-filament standard deviation in the mean $^{53}Cr/^{52}Cr$ ratio for 50 replicates of 0.05‰. Replicate analyses of 21 samples of native water from wells in the Sheep Creek fan and the Surprise Spring area agreed with a mean-square error of 0.17‰ (Fig. 2). Replicate analyses of water from 4 wells at an industrial site near El Mirage, California agreed with a similar precision, despite initial interference in the Cr separation from SO_4^{2-} concentrations as high as 3300.

3.4. Statistical analysis

Correlation coefficients reported in this manuscript are Spearman Rank correlation coefficients and comparison of median values is done on the basis of the Median test (Neter and Wasserman, 1974) using a confidence criterion of $\alpha = 0.05$. Least-squares regression statistics and other statistical results reported in this manuscript were

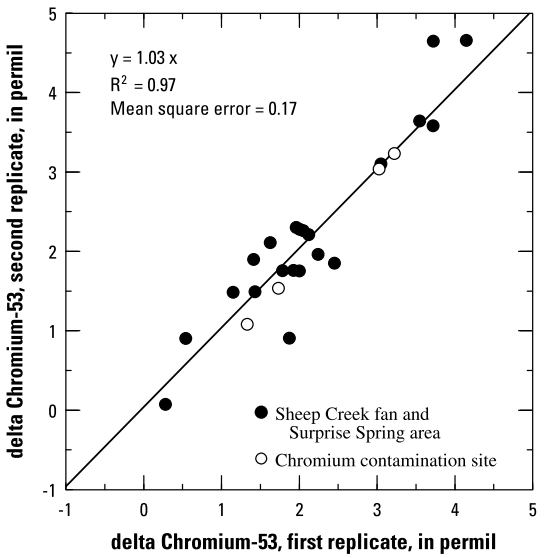

Fig. 2. Comparison of replicate analysis of $\delta^{53}Cr$ from selected samples from the Sheep Creek fan and Surprise Spring area, southern California.

calculated using software from the Statistical Analysis System (SAS).

4. Results and discussion

4.1. Abundance of chromium, and other selected trace elements

The distribution of naturally-occurring Cr and other trace elements in ground-water results from spatial variations in the abundance of these trace elements in aquifer deposits and from geochemical processes that control their concentration and mobility in ground-water. In this study, Cr and selected trace-element abundances were evaluated on the basis of elemental concentrations in minerals that compose aquifer deposits, and on the basis of elemental concentrations on Fe-oxide and Mn-oxide exchange sites on mineral grains. Geochemical controls on the dissolution and mobility of Cr, As, and selected trace elements in ground-water, including pH, redox, and contact time were evaluated.

4.1.1. Source rock and alluvium

Selected samples of source rock collected from the Pelona Schist within the drainage area of Sheep Creek were composed primarily of SiO_2 and Al with smaller amounts of Fe, Mg and Ca in proportions ranging from about 2 to 20% by weight (Table 1). Smaller amounts of Na, K, Ti and Mn also were present. Iron and Mn concentrations listed in Table 1 are higher than concentrations reported by Ehlig (1958) for the Pelona Schist, and sodium concentrations are lower.

Green, crystalline minerals, having the fibrous morphology of actinolite, present within the greenschist facies were identified as an amphibole by X-ray diffraction. The amphibole had less SiO_2 and Al, and more Fe, Mn and Ca than either the gray schist or green schist rock samples consistent with the mafic character of these minerals.

Samples from the gray schist and greenschist facies of the Pelona Schist were analyzed for selected trace elements using Energy-Dispersive X-Ray Fluorescence (EDXRF) and Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP-OES). Chromium was measured at concentrations as high as 1020 ppm in the amphibole using EDXRF (Table 1). The presence of Cr was confirmed through analysis of digested rock using ICP-OES although the measured concentrations were lower than concentrations measured using EDXRF. Nickel was measured at concentrations up to 1020 ppm. High Ni concentrations are commonly observed in rock having high-Cr concentrations (Reimann and Caritat, 1998). Weathered amphibole in samples from the Pelona Schist was characterized by loss of crystal structure, rock integrity, and accumulations of SO_4^{2-}, presumably from oxidation of associated sulfide minerals. Low Cr concentrations in the weathered amphibole suggest that Cr is preferentially removed from the rock by weathering.

Data on the chemical composition of source rock were not collected in the Surprise Spring area because the geology of this area did not indicate the presence of Cr-rich rock.

Alluvial deposits in the Sheep Creek fan and Surprise Spring areas are composed primarily of nonreactive silicate minerals such as quartz, plagioclase, orthoclase and mica, with smaller amounts of amphibole, chlorite, titanite and other minerals (Fig. 3). Chromium and other trace elements of interest in this study were believed to be present primarily in the nonmagnetic mineral fraction having a density greater than 2.8, known as the C-3 fraction. Minerals within that fraction are less abundant and often are not easily detected unless they are separated from the more abundant minerals as described previously in the "Methods" section.

Within the Sheep Creek fan deposits, minerals in the C-3 fraction were primarily within the mica and amphibole groups, and accounted for about 35 and 20% of this fraction, respectively (Fig. 3). Smaller amounts of chlorite, titanite, epidote, apatite and rutile also were present. Chromium-containing minerals such as chromite were not identified in the C-3 mineral fraction.

Chromium substitution in clinozoisite, a mineral within the epidote group, was observed in the C-3 mineral fraction using Scanning Electron Microscopy (SEM) with spectral analysis. However, clinozoisite was considered to be less important as a source of Cr than minerals within the amphibole group because of the smaller abundance of epidote group minerals in the parent rock. Gray (2004) reported Cr substitution within chlorite, but Cr substitution in chlorite was not observed in samples analyzed as part of this study. Fuchsite, a Cr-containing mica mineral, reported to exist within the Pelona Schist in the San Gabriel Mountains near the study area (U.S. Geological Survey, 2003) was not identified in any of the rock or C-3 mineral samples analyzed as part of this study.

Within the Surprise Spring area, the C-3 mineral fraction included titanite and minerals within the

Table 1
Elemental composition of rock samples from Pelona Schist outcrops within the Sheep Creek drainage, San Gabriel Mountains, southern California

Description	Site identification	Elemental oxide concentration, in weight percent									Total
		SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	
Gray schist	1	63	0.76	16.8	5.5	0.10	3.7	4.3	0.4	3.3	98
Weathered gray schist	2	79	0.17	4.18	4.8	0.04	1.4	3.4	4.1	2.0	100
Greenschist	3	65	0.60	13.4	4.0	0.13	2.2	5.1	2.4	0.55	94
Amphibole	4	48	1.3	5.05	9.9	0.15	20	11	4.0	3.6	103
Amphibole	5	60	0.10	2.6	6.8	0.27	20	13	3.2	1.6	108
Weathered amphibole	6	56	1.2	15.0	9.3	0.26	5.4	4.9	0.3	0.03	92
Analytical error, in %		4.15	3.24	4.1	4.09	5.96	2.93	8.89	0.373	1.85	

Description	Site identification	Selected trace element concentration, in parts per million by weight									
		Arsenic		Chromium		Nickel		Vanadium		Uranium	
		EDXRF	ICP	EDXRF	ICP	EDXRF	ICP	EDXRF	ICP	EDXRF	ICP
Gray schist	1	–	–	–	5	–	3.8	–	–	–	–
Weathered gray schist	2	–	–	–	1.3	–	2.8	–	–	–	–
Greenschist	3	–	–	–	4.2	2.7	2.7	–	–	–	–
Amphibole	4	<1	–	1020	155	1020	93	110	–	<4	–
Amphibole	5	<1	–	620	110	450	106	39	–	<4	–
Weathered amphibole	6	<1	–	15	4.6	6	2.6	240	–	<4	–

[Selected trace-element concentrations determined by energy-dispersive X-ray fluorescence (EDXRF) and (or) inductively coupled plasma with optical emission spectroscopy (ICP). Elemental oxide and ICP data from Scripps Institute of Oceanography. EDXRF data from U.S. Geological Survey, Geologic Division, Denver, CO. <, less than. Amphibole identified as actinolite on the basis of crystal morphology or as actinolite/tremolite on the basis of elemental composition. Additional analysis needed for positive identification].

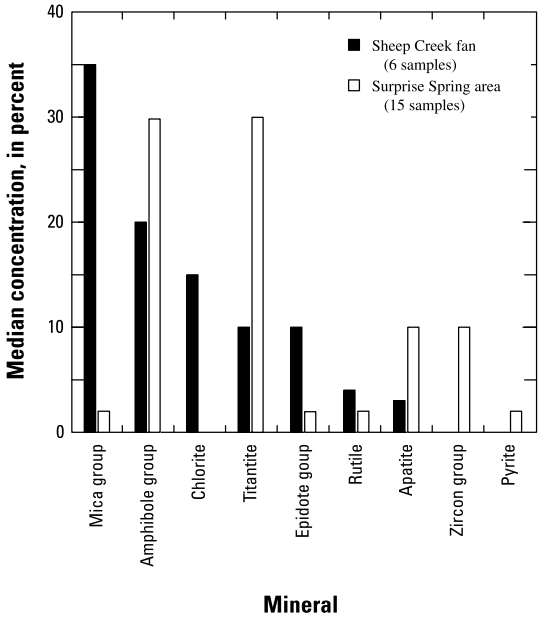

Fig. 3. Mineralogy of the C-3 (non-magnetic, heavy mineral) fraction of alluvial material in the Sheep Creek fan and Surprise Spring areas, western Mojave Desert, southern California.

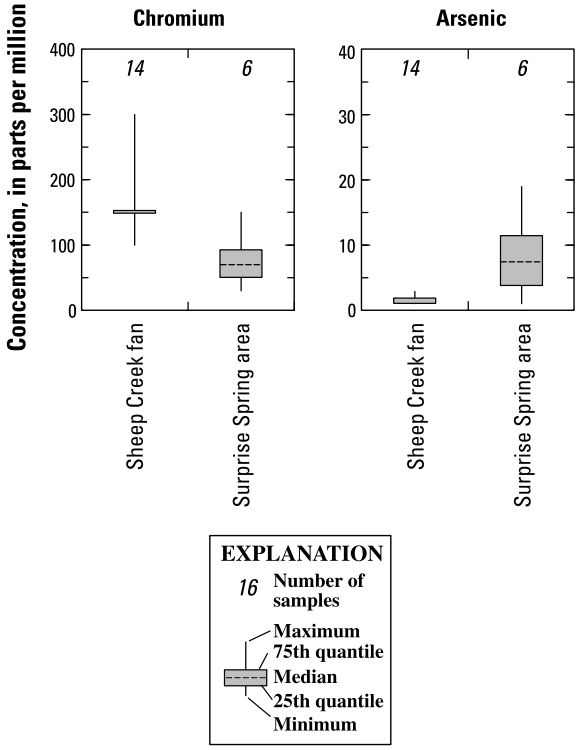

Fig. 4. Concentration of Cr and As in the C-3 mineral fraction of alluvial material from the Sheep Creek fan and Surprise Spring areas, western Mojave Desert, southern California.

amphibole group, with smaller amounts of apatite and zircon (Fig. 3). The lower aquifer underlying the Surprise Spring area contains a greater percentage of alluvium derived from local metavolcanic rook than does the upper aquifer and contains more epidote group and less amphibole group minerals than the upper aquifer. Small amounts of pyrite were present in the C-3 mineral fraction from the lower aquifer. Chromium minerals were not identified in the C-3 mineral fraction from the Surprise Spring area. Amphibole present within the Surprise Spring samples was primarily hornblende, rather than actinolite, and does not contain large amounts of Cr.

Chemical analysis of the C-3 mineral fraction shows that Cr is more abundant in alluvium from the Sheep Creek fan than in alluvium from the Surprise Spring area (Fig. 4). In contrast, As is more abundant in the Surprise Spring area than in the Sheep Creek fan, especially in the lower aquifer system where it may be associated with pyrite present within those deposits. Results from the Sheep Creek fan and Surprise Spring area are consistent with the differences in the source rock mineralogy, and the average elemental abundances reported in the literature for Cr and As in these types of rocks (Reimann and Caritat, 1998).

4.1.2. Extractions from alluvium

Chromium, As and other trace elements sorbed to Fe and Mn oxide coatings on mineral grains are more readily mobilized to ground-water, given suitable geochemical conditions, than trace elements within minerals that dissolve slowly.

Almost all the Cr, As and V from alluvium in the Sheep Creek fan and the Surprise Spring area was in the HCl-extractable fraction. In this fraction, V was more abundant, followed by Cr, As and U. The relative abundances of these trace elements in the HCl-extractable fraction were consistent with their relative abundance in the continental crust (Reimann and Caritat, 1998). Iron and Mn concentrations were several orders of magnitude higher than As, Cr, V or U concentrations (Fig. 5). Chromium, As and V concentrations in the HCl-extractable fraction were positively correlated with Fe and Mn concentrations. On the basis of these data, Mn oxides on the surface coatings of mineral grains are abundant and may be responsible for the oxidation of Cr(III) weathered from rocks and minerals to Cr(VI) (Guha et al., 2000).

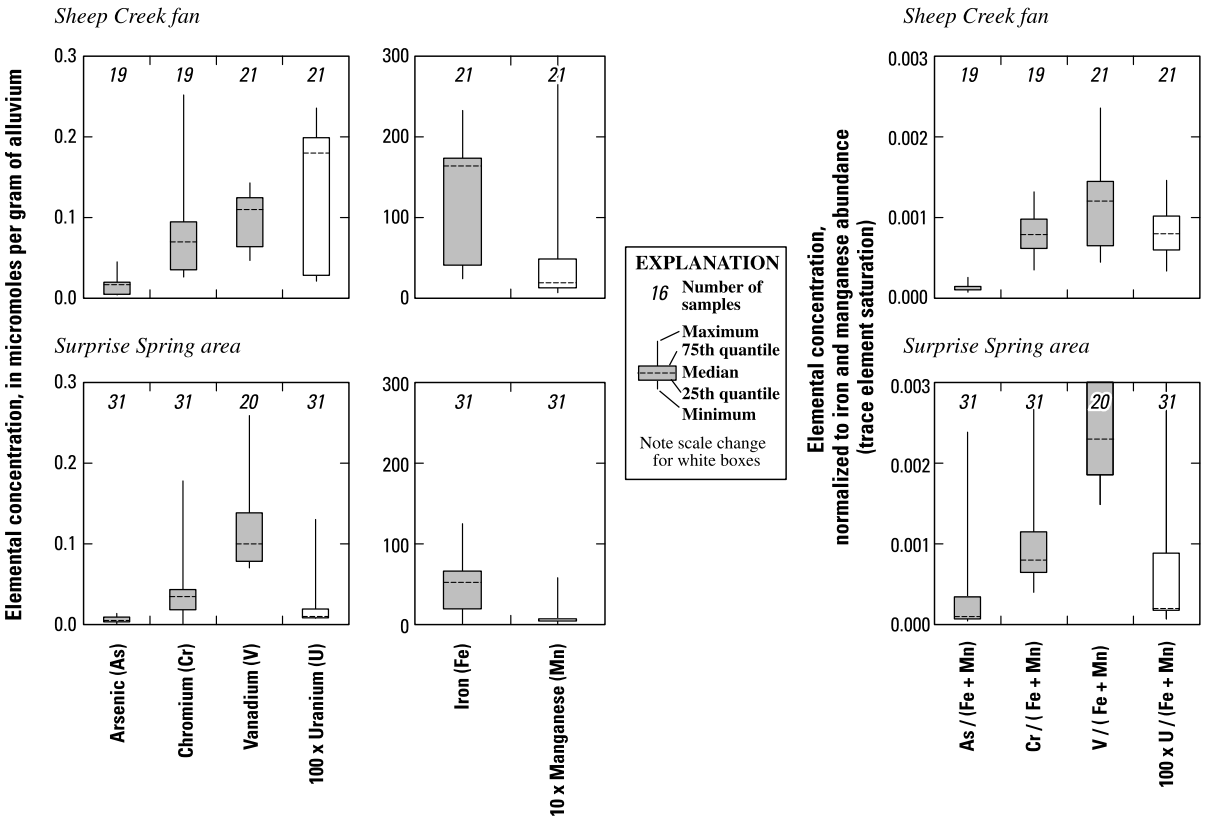

Fig. 5. Concentration of As, Cr and other selected trace elements in extractions from alluvial material from the Sheep Creek fan and Surprise Spring areas of the western Mojave Desert.

The abundance of U in the HCl-extractable fraction was several orders of magnitude lower than the abundance of As even though they have similar abundance in the earth's crust (Reimann and Caritat, 1998). It is unclear if this difference results from local differences in abundance in the source rock, or from differences in the geochemical behavior of U and As. For example unlike As and the other trace elements measured as part of this study, carbonate minerals impose solubility constraints on U in oxic ground-water (Noubactep et al., 2003). Consistent with these solubility constraints, about half of the U in core material and cuttings from the Surprise Spring area was extracted in the KCl-extractable fraction and was presumably associated with carbonate minerals. In addition, unlike other trace elements measured, U concentrations in the HCl-extractable fraction were not significantly correlated with Fe or Mn concentrations in the HCl-extractable fraction.

Median Cr, U, Fe and Mn concentrations in the HCl-extractable fraction were significantly greater in alluvium from the Sheep Creek fan than in alluvium from the Surprise Spring area (Fig. 5). Higher concentrations of Cr, Fe and Mn in HCl extracts result from higher concentrations of these elements in mafic minerals within source rock eroded to form alluvium underlying the Sheep Creek fan.

Trace-element saturation on Fe and Mn exchange sites was calculated by dividing the elemental concentration in the HCl-extractable fraction by the Fe and Mn concentrations in that fraction (Fig. 5). In the absence of mineral solubility constraints, such as those imposed on U solubility by carbonate minerals, trace-element concentrations in oxic, alkaline ground-water may be controlled by exchange with trace elements sorbed on Fe and Mn oxide exchange sites on mineral grains. Therefore, trace-element saturation data may provide a better indicator of the trace-element concentrations expected in ground-water than the total concentrations measured in the HCl-extractable fraction.

Chromium saturation on Fe and Mn exchange sites was similar in alluvium from the Sheep Creek

fan and the Surprise Spring area despite differences in source rock and differences in the total elemental concentration in the HCl extract. If Cr concentrations in oxic, alkaline ground-water are controlled by equilibrium with Fe and Mn exchange sites, similar Cr concentrations may be present in ground-water from both areas. In contrast, As saturation on exchange sites on alluvium from the Surprise Spring area was significantly greater than in the Sheep Creek fan. As a consequence, higher As concentrations may be expected in ground-water from the Surprise Spring area.

Median concentrations of Cr, As, V and U in HCl extractions were significantly greater from core material and cuttings collected on the distal portion of the Sheep Creek fan near El Mirage Lake (dry) than for extractions from core material and cuttings collected from sites near the apex and midfan area Fig. 6). Median concentrations of Fe and Mn also were greater in the distal portion of the fan, possibly because of increased surface area of the finer-grained deposits. Because of the greater abundance of Fe and Mn in the distal portion of the Sheep Creek fan, Cr and V saturation on Fe and Mn exchange sites were less in the distal portion of the fan than in the apex and midfan areas. If Cr concentrations in oxic, alkaline ground-water were buffered by equilibrium with surface exchange sites, concentrations in water from wells would be expected to be less in the distal portion of the Sheep Creek fan than in the apex and midfan sections.

4.1.3. Water from wells

Most water sampled from 157 public supply, irrigation and observation wells in the western part of the Mojave Desert was oxic and alkaline, with a median pH of 8.2. Almost all the Cr was present as Cr(VI). Chromium(VI) concentrations in water ranged from less than the detection limit of 0.2 to 60 μg/L with a median concentration of about 7 μg/L (Fig. 7). Chromium(VI) concentrations were higher in water from wells having a pH > about 7.5 and dissolved O_2 concentrations > about 0.5 mg/L (Fig. 7). Water from 2 wells screened in alluvial

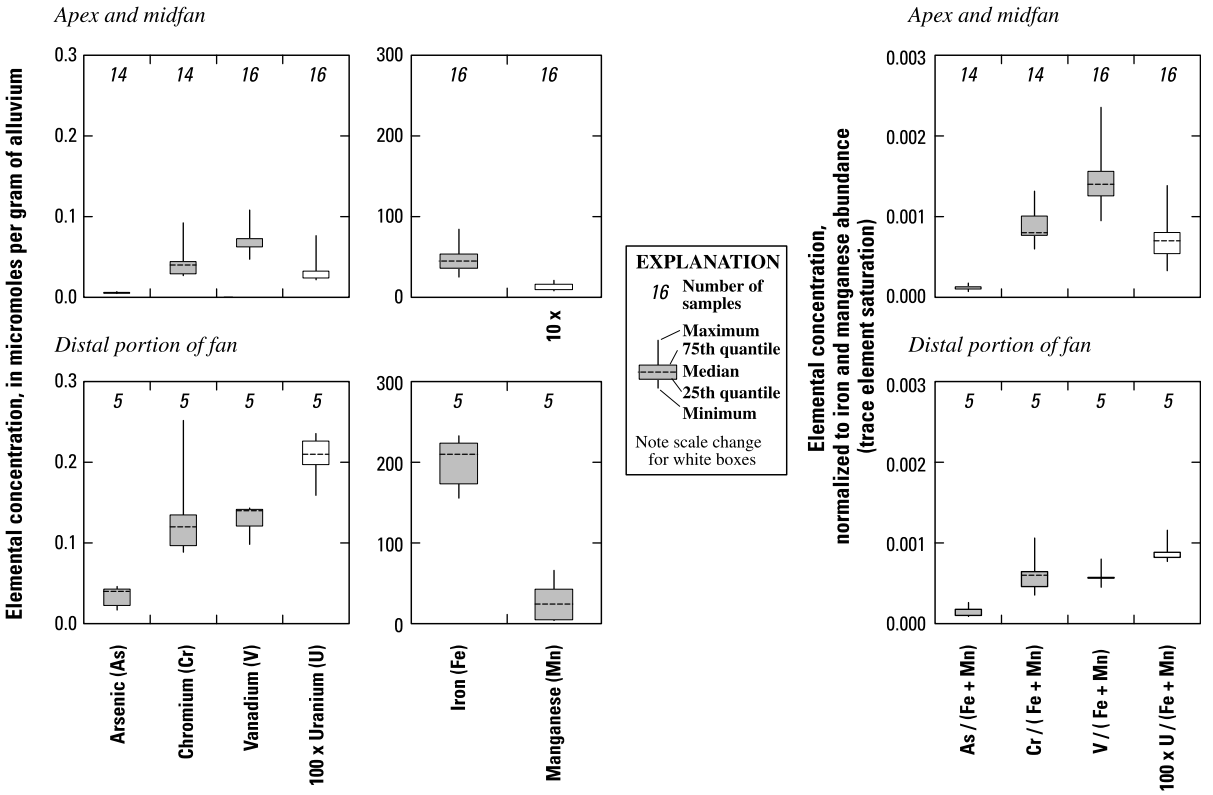

Fig. 6. Concentration of Cr and other selected trace elements from alluvial material in HCl extractions from the apex and distal areas of Sheep Creek fan.

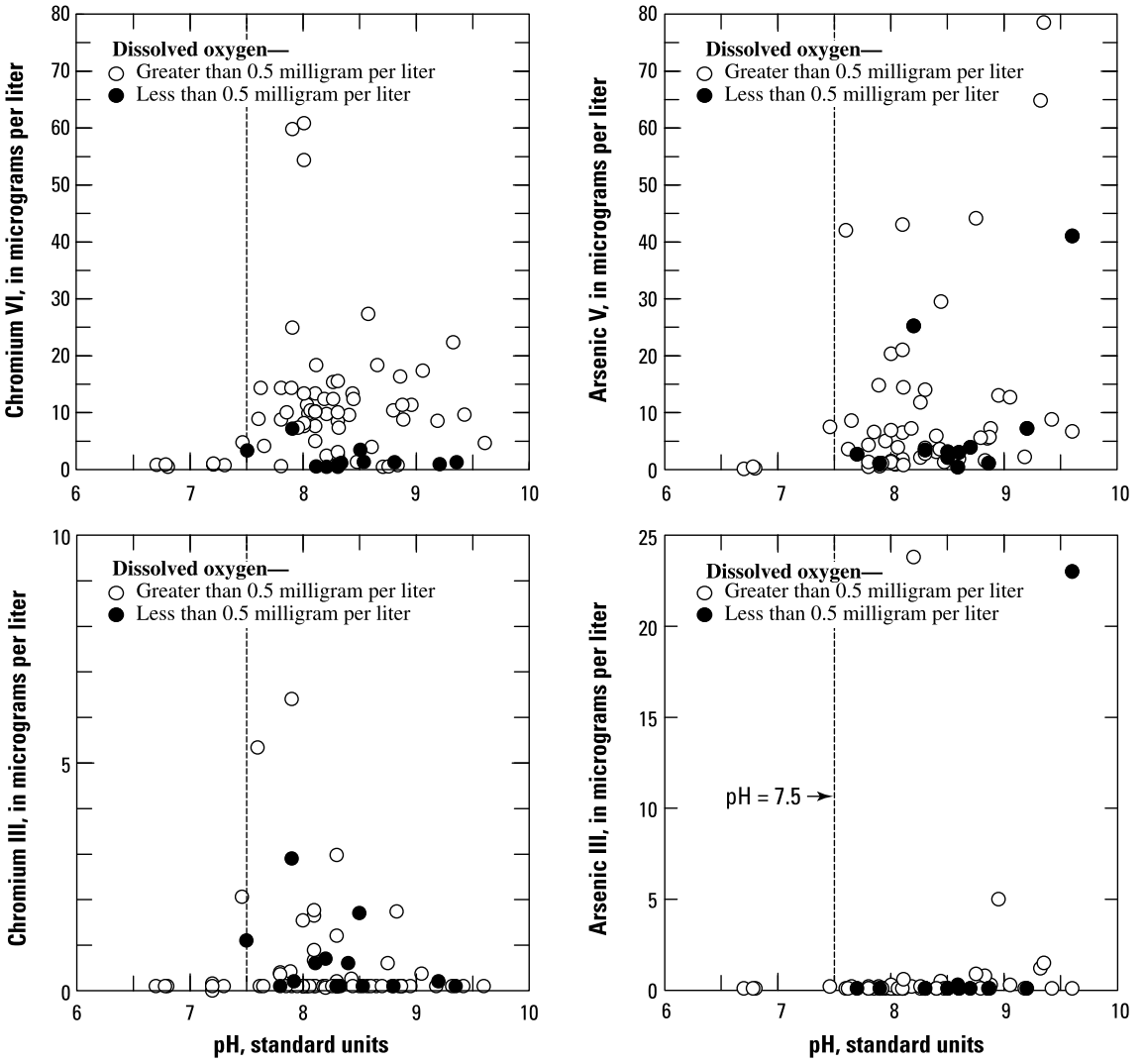

Fig. 7. Chromium(VI) and Cr(III), and As(III) and As(V) concentrations as a function of pH and dissolved O_2 concentrations in water from wells in the western Mojave Desert, 2001–2003.

deposits underlying the Sheep Creek fan exceeded 50 μg/L, the California Maximum Contaminant Level for total Cr. Despite the predominance of Cr(VI), 42% of sampled wells had Cr(III) at concentrations greater than the detection limit of 0.2 μg/L, and 13% had Cr(III) at concentrations greater than 1 μg/L. Surprisingly, Cr(III) concentrations were higher in water from wells having oxic conditions and dissolved O_2 concentrations > about 0.5 mg/L (Fig. 7), suggesting that reduction of Cr(VI) to Cr(III) can proceed before waters go anoxic. Chromium(III) concentrations were higher in water from wells having a pH > about 7.5, presumably because these waters would have had higher Cr(VI) concentrations before becoming anoxic. Chromium(III) concentrations were highest in water from well 6N/7W-28L1 on the Sheep Creek fan and in water from observation wells near 8N/10W-1C2-5 near Rogers (dry) Lake. Water from these wells had comparatively high dissolved O_2 concentrations. Natural reductants in the form of reduced Fe, and organic material within the aquifer would be present at both locations possibly facilitating the reduction of Cr(VI) to Cr(III). The distribution of Cr concentrations in water from wells in the western Mojave Desert shown in Fig. 1 are discussed in greater detail by Ball and Izbicki (2004).

Arsenic, similar to Cr, has oxidized and reduced forms and comparison between the oxidized As(V) and reduced As(III) forms of these elements provides confidence in the Cr(VI) and Cr (III) measurements done as part of this study. Arsenic(V) concentrations in 84 selected wells ranged from < the detection limit of 0.2 to 80 μg/L with a median concentration of about 4 μg/L. Arsenic(V) concentrations were higher in water from wells having a pH > about 7.5 (Fig. 7). Although total As concentrations were generally higher in water from wells having dissolved O_2 concentrations > 0.5 mg/L, high As(V) concentrations also occur in water having low dissolved O_2 concentrations (Fig. 7). Water from 22% of the sampled wells exceeded the USEPA MCL for As of 10 mg/L. Similar to Cr, most As was present in the oxidized form as As(V). However, 16% of sampled wells had As(III) concentrations greater than 0.2 μg/L, and 5% of wells had As(III) at concentrations greater than 1 μg/L. Arsenic(III) concentrations were generally low regardless of pH and dissolved O_2 concentrations (Fig. 7). Arsenic concentrations in water from wells in the western Mojave Desert were discussed by Christensen and Fields-Garland (2001).

The relative abundance of oxidized and reduced forms of Cr and As is consistent with expected results for oxic, alkaline ground-water. More Cr(III) is present in water from wells than As(III) because Cr is more readily reduced than As. In addition, the free energy released from the reduction of Cr(VI) is much greater than the free energy released from the reduction of As(V) (Stumm and Morgan, 1996). As a consequence, reduction of Cr(VI) to Cr(III) may proceed more rapidly when conditions are favorable.

Both Cr(VI) and As(V) concentrations were low near the mountain front where pH was near neutral (Ball and Izbicki, 2004). Chromium(VI) concentrations also were low in water from wells near the downgradient end of long flow paths through alluvial aquifers, especially near ground-water discharge areas along dry lakes where dissolved O_2 concentrations in ground-water also were low. Arsenic(V) concentrations were higher in water from deep wells and in water from wells near dry lakes despite low concentrations of dissolved O_2.

Chromium(VI) concentrations were higher in water from wells in the apex and mid-fan portions of the Sheep Creek fan (Fig. 1). These higher concentrations are consistent with the geologic source of Cr in Pelona Schist eroded from the San Gabriel Mountains and the higher Cr saturation on Fe and Mn oxides on mineral grains in this area (Fig. 6). Concentrations were lower in the distal portion of the fan as a result of decreased in dissolved O_2 concentrations and increased Fe and Mn oxide sorption sites on fine-grained deposits in this area that buffer Cr concentrations in solution (Fig. 6).

Chromium(VI) concentrations in water from some wells in the Surprise Spring area also were high and similar to those in the Sheep Creek fan despite the absence of an obvious geologic source of Cr. Chromium is an abundant element in the earth's crust and Cr saturation on Fe and Mn oxides on mineral grains was similar in the Surprise Springs area and the Sheep Creek fan (Fig. 7). High concentrations in water from wells in granitic alluvium of the Surprise Spring area are consistent with exchange between ground-water and Cr sorbed on Fe and Mn oxides on mineral grains.

Chromium(VI) concentrations increase and then decrease to low concentrations as ^{14}C activity decreases and contact time between water and alluvium increases (Fig. 8). The distribution of data does not reflect kinetics of the exchange reaction between Cr sorbed on Fe and Mn hydroxides and ground-water. Instead the data reflect the competing effects of silicate weathering increasing pH along flow paths, initially increasing the desorption of Cr from exchange sites; followed by gradual consumption of dissolved O_2 by naturally-occurring reductants within the aquifer, ultimately reducing Cr(VI) to Cr(III) and removing it from solution. In contrast, As(V) concentrations increase as ^{14}C activity decreases responding solely to the increases in pH from silicate weathering. This occurs because As(V) reduction to As(III) is less sensitive to the gradual consumption of dissolved O_2 than chromium.

4.1.4. Chromium and trace-element concentrations at the water table

Chromium(VI) and selected trace-element concentrations were evaluated at the water table in the perched aquifer at a site in the distal part of Sheep Creek fan upgradient from agricultural development and from the chemical milling facility near El Mirage, California discussed later in this paper. The site was drilled using the ODEX drilling method (Driscoll, 1986), which does not use water as a drilling fluid. Cores were collected from about 7 m above the water table to about 3 m below the water table which was about 29 m below land surface. Deeper core material was collected at selected

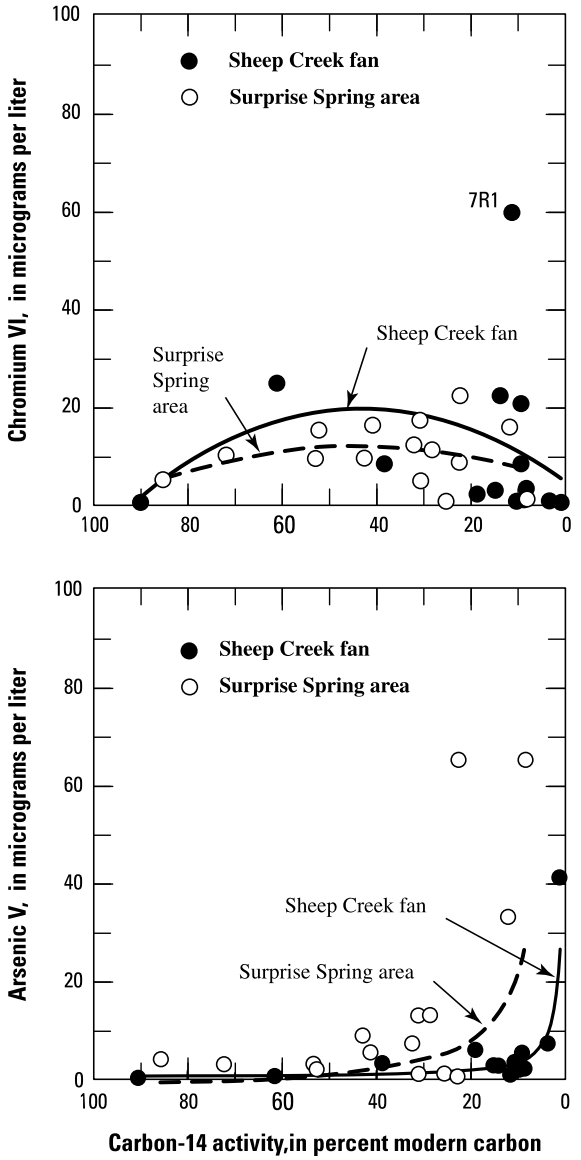

Fig. 8. Chromium(VI) and As(V) concentrations in water from wells as a function of ^{14}C activity and ground-water age in the Sheep Creek fan and Surprise Spring area, western Mojave Desert, southern California.

intervals from an adjacent borehole drilled using reverse mud rotary. A water-table well, 6N/7W-27B8, was installed in the ODEX borehole and 3 deeper wells, 6N/7W-27B5-7, were installed in the adjacent mud-rotary hole. The deepest well, 27B5, was installed in the underlying deep aquifer.

Core material was squeezed in a hydraulic press (Manheim et al., 1994) in the field to extract water. Core material collected more than about 5 m above the water table was too dry to extract water using this approach. Several cores collected less than 3 m above the water table were saturated when extracted from the core barrel. Analysis of geophysical logs and declines in water levels from nearby wells (Smith, 2003), suggest that the material from which water was extracted was beneath the predevelopment water table and was saturated prior to pumping in the area. Extracted water was analyzed in the field for pH and specific conductance, and in the laboratory for Cl^-, SO_4^{2-}, NO_3^-, Cr, As, V and U. Oxidized and reduced forms of Cr and As were not measured.

The pH of water extracted from core material ranged from 7.5 to 8.5 and pH was greater above the water table than in the saturated zone (Fig. 9). The specific conductance ranged from 476 to 1780 μS/cm and was highest in water extracted from a 0.6-m-thick lens at the water-table surface. Chloride, SO_4^{2-} and NO_3^- concentrations (not shown on Fig. 9) were correlated with specific conductance and also were higher near the water-table surface. Given the dry conditions in the overlying unsaturated zone, the high specific conductance water at the water-table surface probably resulted from irrigation-return, or seepage, that moved laterally to the site from nearby agriculture or septic systems.

Chromium concentrations were as high as 13 μg/L in the unsaturated zone above the water table where pH was high and oxic conditions prevailed (Fig. 9). The Cr concentrations in water squeezed from core material near the water table and in water from well 27B8 screened at the water table were lower, about 5 μg/L. Chromium concentrations in water squeezed from core material decreased rapidly with depth in the saturated zone and Cr concentrations in water from wells 27B5-7 were less than the detection limit of 0.8 μg/L. In contrast to Cr, concentrations of As, V and U were highest in the upper 0.6 m of the saturated zone and appeared to be associated with greater specific conductance and soluble salt concentrations. These trace elements may have been mobilized by irrigation-return or septage infiltrated through the unsaturated zone and then moved laterally to the site, in the same manner as Cl^- and soluble salts.

Low Cr concentrations in water from wells 6N/7W-27B5-7 are consistent with low dissolved O_2 concentrations measured in water from those wells. Wells 27B5-7 are upgradient of other wells sampled in the perched aquifer near El Mirage and are presumably representative of background water quality. However, if the observation wells at a

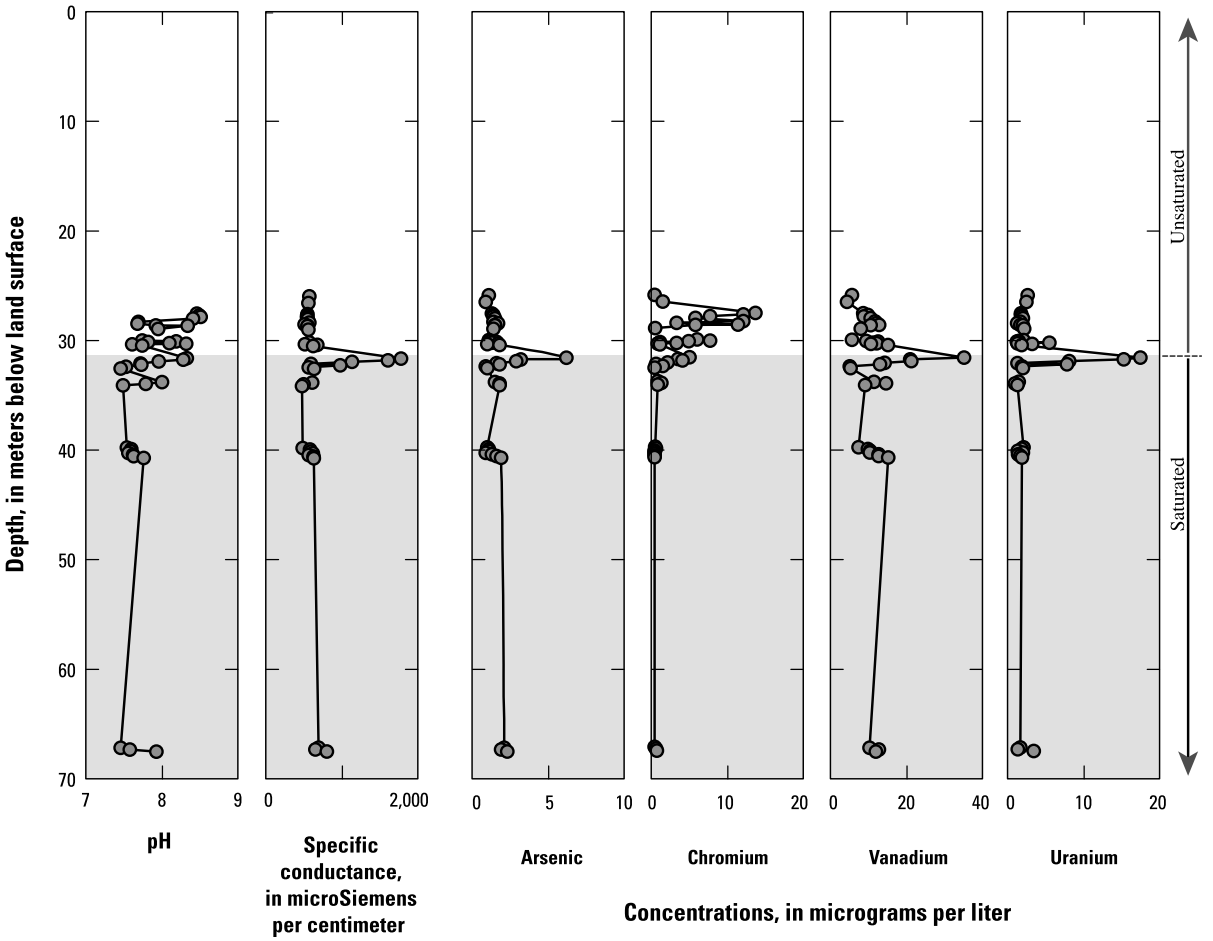

Fig. 9. pH, specific conductance, Cr and selected trace-element concentrations extracted from core material collected at the water table and within the saturated zone, Sheep Creek fan upgradient from El Mirage, western Mojave Desert, southern California.

chemical milling facility and wells 6N/7W-25M2 and 24E1 near that facility are excluded; samples collected from the 19 wells in the "perched aquifer" near El Mirage have dissolved O_2 concentrations ranging from <0.2 to 6.1 with a median concentration of 1.7 mg/L. Chromium(VI) concentrations in these wells ranged from <0.2 to 15 μg/L with a median concentration of 6.0 μg/L. Similar Cr(VI) concentrations were reported for the perched aquifer by Balderman Consulting, Inc. (2001).

A possible explanation for the difference in Cr concentrations between samples collected from wells 27B5-7 and other wells in the perched aquifer is that the other wells yield most of their water from thin, oxic zones near the water table that have high Cr concentrations. It also is possible that other processes aerated water from these wells and subsequently increased Cr(VI) concentrations. Processes that could aerate water from wells include recharge from irrigation-return water having high dissolved O_2 concentrations, or the repeated lowering and raising of the water table during pumping.

4.2. Chromium Isotopic composition of water from wells

The average $\delta^{53}Cr$ composition of the earth's crust is about 0‰ (Shukolyukov and Lugmair, 1998; Ellis et al., 2002). This value is believed to be reasonably constant and has been reported for Cr in basaltic rocks (Shukolyukov and Lugmair, 1998; Ellis et al., 2002), in minerals such as pyroxene, garnet (Lugmair and Shukolyukov, 1998; Shukolyukov and Lugmair, 1998), and chromite (Flesch et al., 1960; Shiraki, 1978) (although the precision of measurements from different studies has varied). The $\delta^{53}Cr$ composition measured using TIMS in Cr-containing amphibole from the study

area also was 0‰ (Chris MacIsaac, Scripps Institute of Oceanography, pers. comm., 2004).

The δ^{53}Cr compositions of native (uncontaminated) water from 32 sampled wells ranged from 0.7 to 5.1‰ (Table 2). This is similar to the range for native ground-water of 1.1 to 5.8‰ reported by Coplen et al. (2002). The δ^{53}Cr composition of water from sampled wells was significantly fractionated with respect to the δ^{53}C composition of the earth's crust. Reductive fractionation may occur either on the surface of mineral grains after weathering prior to Cr entering solution, or it may occur in solution as dissolved O_2 concentrations decline and Cr is removed from solution as Cr(III).

4.2.1. Sheep Creek fan

The δ^{53}Cr composition of native water from 14 wells sampled in the Sheep Creek fan ranged from

Table 2
Field paramenters, total chromium, chromium VI, chromium III, and delta chromium-53 (δ^{53}Cr) values for the Surprise Spring area, and the Sheep Creek fan, western Mojave Desert, southern California

State well number	Well depth (m)	Date	pH (standard units)	Specific conductance (μS/cm)	Dissolved oxygen (mg/L)	Chromium			Delta chromium-53		
						Cr(T) (μg/L)	CrVI (μg/L)	CrIII (μg/L)	Replicate 1 (‰)	Replicate 2 (‰)	Average (‰)
Sheep Creek fan (recharge area, apex and midfan areas, and deep aquifer)											
4N/6W-4D1	335	6/4/02	7.9	538	<0.2	3.0	1.9	1.1	4.1	4.6	4.4
4N/7W-33J1	137	6/4/02	6.8	957	5.2	0.3	<0.2	<0.1	2.3	–	2.3
5N/7W-14A1	–	6/6/02	8.3	511	3.6	7.8	8.1	<0.1	3.5	3.6	3.6
5N/7W-24D3	201	6/4/02	8.5	514	<0.2	–	–	<0.1	2.2	1.9	2.1
5N/7W-28L1	191	6/3/02	7.9	527	2.2	31	25	6.4	1.5	–	1.5
5N/7W-7R1	–	6/6/02	7.9	498	1.7	56	59	<0.1	2.0	2.3	2.1
6N/7W-14K1	174	6/5/02	8.4	876	0.5	2.5	1.9	0.6	2.2	–	2.2
[1/]6N/7W-26J2	184	6/5/02	8.3	702	1.2	3.9	2.7	1.2	5.1	–	5.1
Sheep Creek fan (''perched'' aquifer)											
6N/7W-24D1	30	6/3/02	7.8	531	–	9.3	8.3	1.0	3.7	4.6	4.2
6N/7W-24E2	46	6/6/02	7.70	554	–	22	22	0.3	1.9	1.7	1.8
6N/7W-25M2	–	5/18/01	8.00	1520	6.1	–	55	–	2.0	2.3	2.1
6N/7W-25M2	–	6/5/02	8.0	1520	6.1	60	60	<0.1	2.3	–	2.3
6N/7W-27B8	34	1/23/03	8.6	513	12	8.9	8.6	0.3	3.1	–	3.1
6N/7W-29N2	91	6/3/02	7.5	513	<0.2	4.0	3.0	1.1	4.0	–	4.0
Surprise Spring area (upper aquifer)											
3N/7E-32D4	201	5/14/01	9	.12	4.6	10	11	<0.1	2.1	2.2	2.2
3N/7E-32D5	165	5/14/01	8.9	320	–	4.2	4.6	<0.1	2.4	1.8	2.1
3N/7E-32D6	113	5/14/01	8.2	320	2.8	11	12	<0.1	2.0	1.7	1.9
Surprise Spring area (lower aquifer and Deadman Lake area)											
2N/7E-10D1	274	5/15/01	9.3	267	6.2	22	22	0.0	1.2	–	1.2
2N/7E-10D3	160	5/15/01	8.7	224	3.4	16	18	<0.1	2.0	2.2	2.1
2N/7E-10D4	128	5/15/01	8.6	214	12	–	27	–	1.7	–	1.7
3N/8E-28P1	120	5/14/01	7.8	1649	2	8.8	8.4	0.4	1.4	1.5	1.4
3N/8E-28P2	55	5/14/01	7.8	1605	1.7	14	14	0.4	1.5	–	1.5
3N/8E-28P3	26	5/14/01	7.6	.413	3.4	13	14	<0.1	1.3	–	1.3
3N/8E-31J2	97	5/16/01	–	450	–	9.8	9.6	0.3	3.7	3.6	3.6
3N/8E-31J3	76	5/16/01	–	423	–	9.7	9.7	<0.1	3.0	3.1	3.1
Other areas in the western Mojave Desert											
2N/9E-32R3	24	5/15/01	7.5	2690	5.8	6.5	4.2	2.1	0.3	0.1	0.2
4N/4W-36R2	24	6/6/02	8.73	199	–	22	22	<0.1	0.5	0.9	0.7
8N/10W-1C2	213	6/6/02	8.3	333	3.2	13	–	–	1.8	1.7	1.8
8N/10W-1C3	210	6/6/02	8.1	416	5.4	9.0	7.3	1.8	1.6	2.1	1.9
8N/10W-1C4	183	6/7/02	8.0	383	4.2	8.8	–	–	1.4	1.9	1.6
8N/10W-1C5	152	6/5/02	8.1	354	7.4	10	–	–	1.1	1.5	1.3
1N/7E-21H1	262	12/3/01	8.5	231	–	–	33	<0.1	1.9	0.9	1.4

[All chromium values dissolved. Cr(T), total chromium (Cr VI + Cr III); Cr VI, hexavalent chromium; Cr III, chromium-III; m, meters, μS/cm, microsiesmens per centimeter; mg/L, milligrams per liter; μg/L, micrograms per liter; ‰, parts per thousand].

1.5 to 5.1‰, with a median composition of 2.3‰ (Table 2). The values were significantly greater than values measured in water from wells elsewhere in the Mojave Desert, and suggest that greater fractionation of Cr has occurred in ground-water from aquifers underlying the Sheep Creek fan.

The δ^{53}Cr composition of water from well 4N/7W-33J1 in the alluvium-filled canyon of Sheep Creek in the San Gabriel Mountains was 2.3‰ and the Cr(VI) concentration was 0.3 μg/L (Table 2). Even though the water from this well contained high concentrations of dissolved O_2 (5.2 mg/L), low Cr (VI) concentrations and is at the beginning of the flow path, δ^{53}Cr composition indicated that the water sampled from this well had already undergone fractionation relative to the δ^{53}Cr composition of the parent rock. It is possible that reduced Fe or graphite disseminated within the Pelona Schist and alluvium eroded from the schist may have reduced Cr(VI) to Cr(III) on the surface of mineral grains, fractionating Cr on aquifer materials before it entered solution.

The δ^{53}Cr composition of water from well 5N/7W-7R1 downgradient from well 33J1 was 2.1‰ and the Cr(VI) concentration was 60 μg/L. Water from well 7R1 showed no change in δ^{53}Cr composition compared to water from well 4N/7W-33J1 despite increased Cr(VI) concentrations (Fig. 10). Although dissolved O_2 concentrations decreased from 5.2 to 1.7 mg/L between wells 33J1 and 7R1, water from well 7R1 was oxic and reductive fractionation of Cr in solution should not have been extensive. The observed δ^{53}Cr composition of water in well 7R1 is believed to be the result of fractionation of Cr on the aquifer material prior to entering solution, similar to processes that occurred at well 33J1.

The Cr(VI) concentrations in water from wells decreased and δ^{53}Cr values increased downgradient from well 5N/7W-7R1 toward wells 6N/7W-26J2 in the deep aquifer and wells 6N/7W-29N2, and 24D1 in the perched aquifer (Table 2). Fractionation of Cr isotopes occurred as Cr(VI) was reduced to Cr(III) and removed from solution. Assuming water from well 7R1 was representative of the initial Cr(VI) concentration and initial δ^{53}Cr composition, reductive fractionation of Cr within the perched aquifer was calculated from the following:

$$(R_{samp}/R_o) = (C/C_o)^{\alpha-1} \quad (1)$$

where

R_{samp} is the Cr^{53}/Cr^{52} ratio in the sample water
R_o is the initial Cr^{53}/Cr^{52} ratio
C is the Cr concentration in the sample water
C_o is the initial Cr concentration, and
α is the Cr fractionation factor, 0.9965 (Ellis et al., 2002). Recent work (Kitchen et al., 2004) suggests there may be some variation in this number not addressed in this paper.

The Cr^{53}/Cr^{52} ratio in the sample water (R_{samp}) was calculated from the δ^{53}Cr value, in ‰, from the following:

$$R_{samp} = (\delta^{53}Cr \cdot R_{std})/1000) + R_{std} \quad (2)$$

where

R_{std} is the Cr^{53}/Cr^{52} ratio in the National Institute of Standards and Technology Standard Reference Material 979, 0.113418.

The calculated Cr(VI) concentrations and δ^{53}Cr values from well 7R1 define the maximum limit of Cr concentrations and δ^{53}Cr isotopic compositions expected in the perched aquifer underlying the Sheep Creek fan. Water from most wells in the perched aquifer (and water from deep wells elsewhere on the Sheep Creek fan, such as 4N/6W-4D1) have lower Cr(VI) concentrations and higher δ^{53}Cr values and are consistent with a 25 to 50% reduction in natural Cr(VI) concentrations (Fig. 10). However, initial Cr(VI) concentrations in water from these wells must have been lower than those measured in water from well 7R1, or Cr(VI) was removed by other processes that do not result in fractionation, such as sorption of Cr on the increasingly abundant Fe and Mn oxides present on the surface of mineral grains within the fine-grained deposits that compose the perched aquifer (Fig. 6).

Water from wells 6N/7W-24E2 and 25M2 in the perched aquifer had higher Cr(VI) concentrations and lower δ^{53}Cr values than expected on the basis of data from other wells sampled in the perched aquifer (Table 2). Although different in their chemical and isotopic composition from other wells in the perched aquifer, water from wells 24E2 and 25M2 were within the expected range for water from wells on the Sheep Creek fan. The data suggest that either reductive fractionation and removal of Cr(VI) from solution has not occurred, or that the Cr has originated from a different source and the δ^{53}Cr

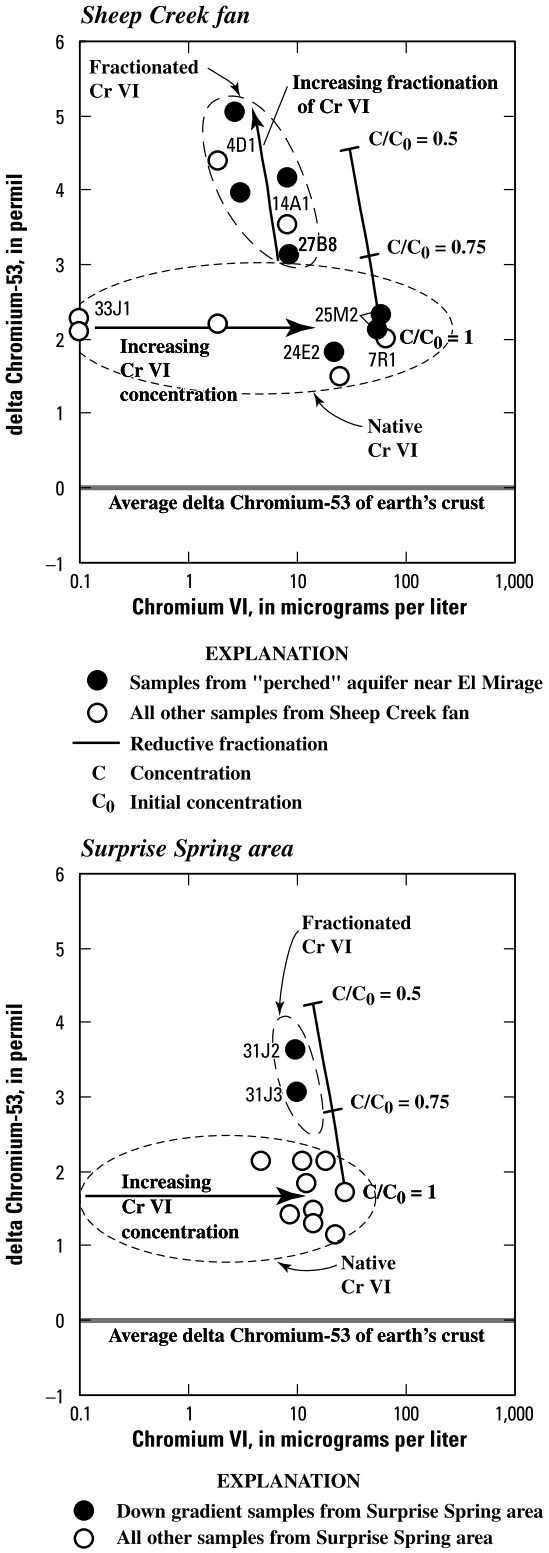

Fig. 10. Chromium(VI) concentrations and δ^{53}Cr values in water from wells in the Sheep Creek fan and Surprise Spring area, western Mojave Desert, southern California.

composition evolved along a different geochemical pathway from other wells sampled in the perched aquifer. The possible origin of the δ^{53}Cr composition of water from these wells is discussed in greater detail later in this paper.

4.2.2. Surprise Spring area

The δ^{53}Cr composition of 11 wells sampled in the Surprise Spring area ranged from 1.2 to 3.6‰ with a median composition of 1.9‰. Most δ^{53}Cr values in the Surprise Spring area ranged from 1.3 to 2.2‰ (Table 2). The median Cr isotopic composition was significantly different from the median Cr δ^{53}Cr composition in water wells from the Sheep Creek fan. The difference probably results from the fewer natural reductants (either reduced Fe or graphite in the parent rock of the Surprise Spring area) and less subequent reductive fractionation of Cr isotopes compared to the Sheep Creek fan.

High δ^{53}Cr values were measured in water from observation wells 3N/8E-31J2 and 31J3 (Table 2, Fig. 10). These values are consistent with reduction of Cr(VI) to Cr(III) in the same manner as in the perched aquifer underlying the Sheep Creek fan. Water from most other wells in the Surprise Spring area was oxic and not greatly fractionated by the reduction of Cr(VI) to Cr(III) and the subsequent removal of Cr(III) from solution.

4.2.3. Other areas in the western Mojave Desert

The δ^{53}Cr composition of water from well 4N/4W-36R2 in the Victorville fan, east of the Sheep Creek fan (Fig. 1), was 0.7‰ (Table 2). Although lower than values from the Sheep Creek fan or the Surprise Spring area, given an analytical precision of 0.15‰, this value is fractionated relative to the average δ^{53}Cr composition of 0‰ in the earth's crust. The Victorville fan contains some alluvium eroded from the Pelona Schist in the San Gabriel Mountains, possibly explaining the relatively high Cr(VI) concentration in water from the well, 22.4 μg/L.

The δ^{53}Cr compositions of water from wells 8N/10W-1C2-5, completed in alluvium weathered from granitic rock near Rogers Lake (dry), ranged from 1.3 to 1.8‰ (Fig. 1) and were similar to the δ^{53}Cr composition of water from wells in the Surprise Spring area. Despite the location of the wells near a dry lake, dissolved O_2 concentrations in water from these wells ranged from 3.2 to 7.4 mg/L (Table 2) and reduction of Cr(VI) to Cr(III) and subsequent fractionation of Cr isotopes did not occur.

These values are within the range of δ^{53}Cr compositions expected for granitic alluvium on the basis of data from the Surprise Springs area.

Water from well 2N/9E-32R3 located near Mesquite Lake (dry) (Fig. 1), in an area receiving treated municipal wastewater from the Marine Corps base, had a δ^{53}Cr composition of 0.16‰ and was not significantly fractionated with respect to the composition of the earth's crust. Although Cr(VI) concentration in water from well 32R3 was only 4.2 μg/L, δ^{53}Cr compositions near 0‰ are indicative of anthropogenic Cr (Ball, 1996; Ball and Bassett, 2000; Ball et al., 2001; Ellis et al., 2002, 2004) and the Cr(VI) in water from well 32R3 may have originated from the discharge of treated wastewater. Water from well 32R3 also had unusual chemistry compared with that of water from other wells sampled, including the highest specific conductance (from the dissolution of soluble salts from the dry lake), the lowest pH, and almost one-third of the Cr was present as Cr(III) (Table 2).

Near zero δ^{53}Cr values of 0.1 and 0.2‰, were previously reported in water from two wells at a contamination site near Hinkley, California. (Ball et al., 2001). The Cr(VI) concentrations of water from these wells were 1300 and 1800 μg/L, respectively. Comparison of these data with native water from wells sampled as part of this study suggests that the δ^{53}Cr composition of water from wells may be useful in defining the extent of anthropogenic Cr(VI) in areas having high natural background concentrations.

4.3. Use of chromium isotopes to identify anthropogenic chromium

Water containing neutralized acids and other waste from the chemical milling of metal parts was discharged between 1967 and 1980 to a 0.9-ha unlined pond at an industrial facility near El Mirage, California where it infiltrated to the underlying ground-water (Fig. 11). Between 1980 and 1987, process water from the facility was discharged to a 0.3 ha lined pond constructed within the unlined pond, where it evaporated (Aerochem Inc., 1996). After 1987 process water was not discharged at the site. Although some data are available, the total volume and chemical composition of the discharge is not precisely known (Balderman Consulting, Inc., 2004). In addition to neutralized acids and other wastes detected onsite, Cr also is present in ground-water at the site at

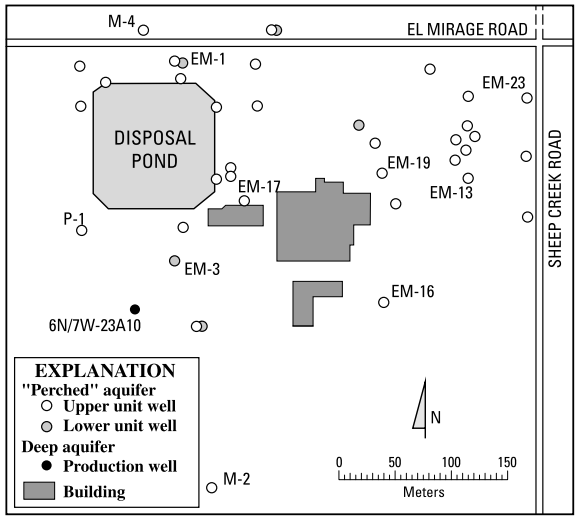

Fig. 11. Waste-disposal ponds, manufacturing facilities, and selected observation wells at an industrial site near El Mirage, western Mojave Desert, southern California.

concentrations as high as 330 μg/L. The location, timing and volume of Cr releases are not known, but the Cr may have been released within the chemical milling facility rather than as a discharge to the ponds (Balderman Consulting, Inc., 2004). It is difficult to determine the extent of Cr from industrial process at the site given the uncertain, and complex, history of industrial discharges, and the natural background concentrations of Cr in nearby wells.

The perched aquifer at the site has been divided into an upper unit about 0 to 20 m below land surface and a lower unit between 30 and 38 m below land surface (Balderman Consulting, Inc., 2004). The upper and lower units are separated by fine-grained deposits and underlain by alluvial deposits of the regional aquifer. Depth to the water table was about 10.5 m and water levels were lower in deeper wells, suggesting a downward gradient at the site. Water-level data show that during this study (2002), the water table sloped to the E/NE in the upper unit (Balderman Consulting, Inc., 2004), and to the NE in the lower unit. Historical data suggest that in the past the water table in the upper unit also may have sloped toward the north (Balderman Consulting, Inc., 2004) although the water table gradient when waste was being discharged to the pond is not known.

The specific conductance of 8 wells in the upper unit ranged from 2380 to 6180 μS/cm and pH values ranged from 7.1 to 7.7. The major-ion

composition of water from these wells showed greater Cl^-, SO_4^{2-} and Ca concentrations compared to native water (Fig. 12). In addition to industrial discharges, water-quality at the site also was affected by irrigation-return from nearby agriculture that may account for some of the higher specific conductance values and some of the differences in major-ion chemistry compared to native water. The specific conductance of water from two wells completed in the lower unit, EM-1 and EM-3, were lower than those of water from wells in the upper unit and are similar to background values. Although the specific conductance of water from well EM-1 was slightly elevated, the major-ion data suggest that water from this well could be a mixture of native water and water discharged at the site (Fig. 12).

Waste discharged at the site was partly evaporated before infiltrating into the subsurface and the $\delta^{18}O$ and δD composition of water from wells at the site plots to the right of the meteoric water line along an evaporative trend line (Fig. 13). Recharge from irrigation-return from nearby agriculture also may have altered the $\delta^{18}O$ and δD composition of water from wells; however, the extent of evaporation suggested by the shift in the $\delta^{18}O$ and δD composition of water from observation wells at the site is greater than the extent of evaporation

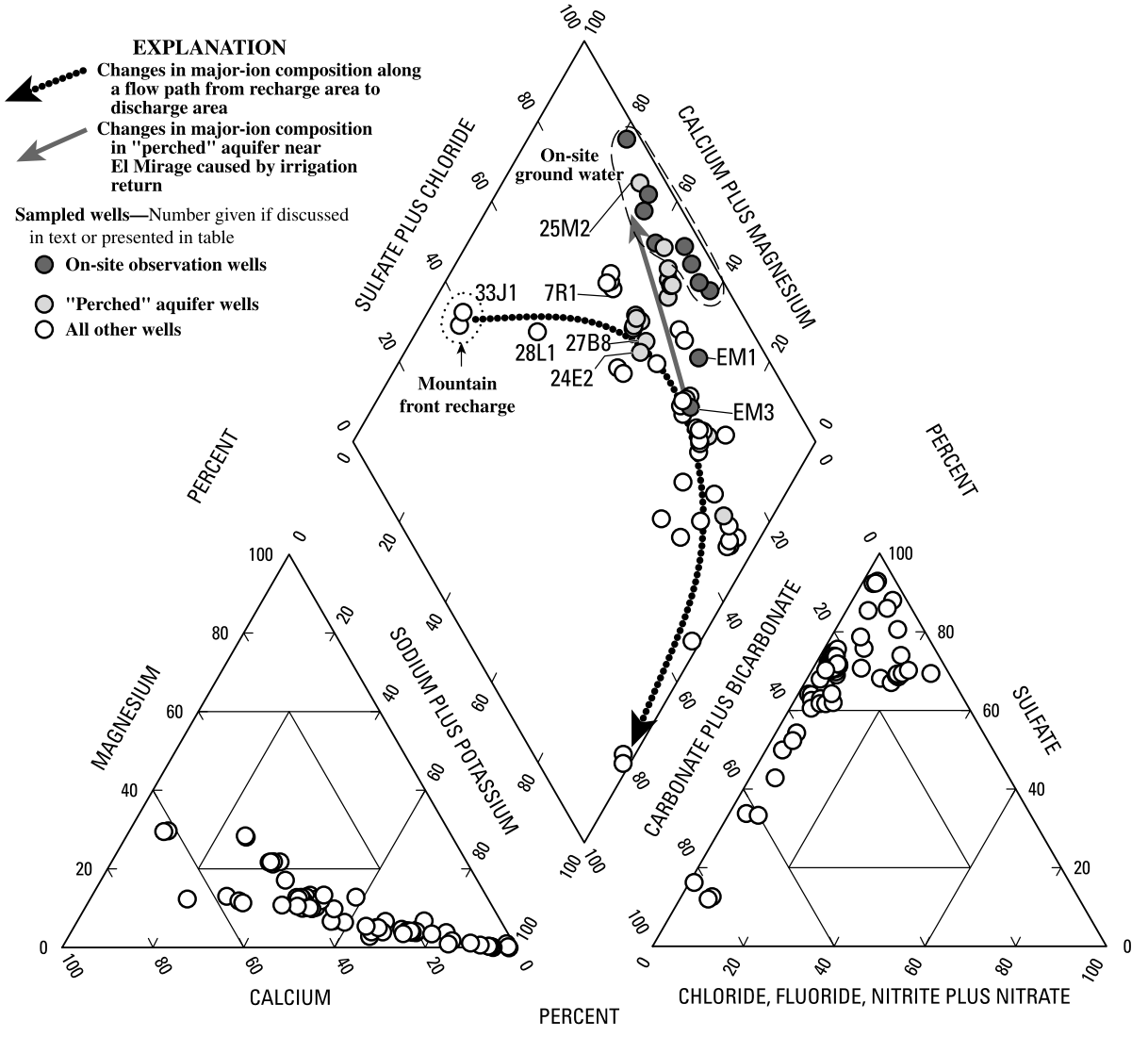

Fig. 12. Major-ion composition of water from wells on the Sheep Creek fan, western Mojave Desert, southern California, 1993–2003.

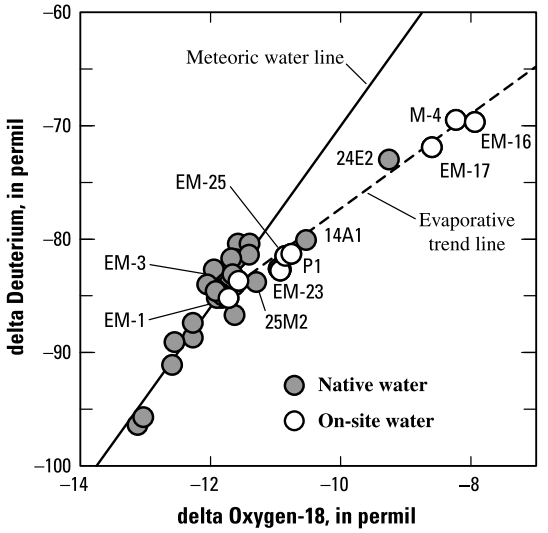

Fig. 13. δ^2H as a function of the $\delta^{18}O$ composition of water from wells in the Sheep Creek fan, western Mojave Desert, southern California.

in water from wells sampled elsewhere in the perched aquifer.

Chromium concentrations in water from 8 upper unit wells sampled at the site ranged from 29 to 310 μg/L (Table 3). Despite the presence of dissolved O_2 in water from sampled wells, Cr(III) concentrations were as high as 23 μg/L. The highest Cr(VI) and Cr(III) concentrations were in water from wells EM-13 and EM-19 north of the chemical milling facility. The lowest Cr(VI) concentrations at the site were in water from the lower unit wells EM-1 and EM-3. However, the Cr(VI) concentrations of 14 and 20 in water from these wells were greater than the median Cr(VI) concentration of 6 μg/L in water from wells elsewhere in the perched aquifer. These concentrations also were greater than expected given low dissolved O_2 and Cr(VI) concentrations less than the detection limit of 0.2 μg/L in the background wells 6N/7W-27B6 and 7 that were completed in the lower unit at similar depths to EM-1 and EM-3.

The $\delta^{53}Cr$ composition of water from the 8 upper unit wells at the chemical milling site ranged from –0.1 to 2.0‰ (Table 3). All values in the upper unit at the chemical milling site were lower than $\delta^{53}Cr$ values elsewhere in the perched aquifer. The lowest value, in water from well EM-16, was not significantly fractionated relative to the average $\delta^{53}Cr$ composition of the earth's crust and relative to the presumed isotopic composition for Cr released at the site of 0‰. The highest $\delta^{53}Cr$ value was 2.0‰ in water from well P1.

The $\delta^{53}Cr$ compositions of water from the lower unit wells within the perched aquifer, EM-1 and EM-3, were heavier (3.2 and 3.0‰, respectively). These values were similar to the $\delta^{53}Cr$ composition in of wells elsewhere in the perched aquifer. These higher (heavier) values also may have resulted from fractionation of anthropogenic Cr during reduction of Cr(VI) to Cr(III). High concentrations

Table 3
Field paramenters, total chromium, chromium VI, chromium III, and delta chromium-53 ($\delta^{53}Cr$) values at a chemical milling facility near El Mirage, western Mojave Desert, southern California

Well number		Date	pH (Standard units)	Specific conductance (μS/cm)	Dissolved oxygen (mg/L)	Chromium			Delta chromium-53		
						Cr(T) (μg/L)	CrVI (μg/L)	CrIII (μg/L)	Replicate 1 (‰)	Replicate 2 (‰)	Average (‰)
"Perched" aquifer-upper unit											
6N/7W-23A EM-1	17.6	6/5/02	7.4	4850	7.3	330	310	20	0.5	–	0.5
6N/7W-23A EM-1	19.2	6/5/02	7.5	3350	2.9	35	31	4.0	−0.1	–	−0.1
6N/7W-23A EM-1	21.8	6/3/02	7.5	6070	6.5	35	31	3.6	1.1	–	1.1
6N/7W-23A EM-1	19.3	6/4/02	7.4	3440	5.5	130	110	20	1.9	–	1.9
6N/7W-23A EM-2	18	6/4/02	7.5	4920	–	31	29	2.4	1.1	1.3	1.2
6N/7W-23A M2	22.1	6/5/02	7.7	2380	5.1	39	37	<0.1	1.5	1.7	1.6
6N/7W-23A M4	37.2	6/5/02	7.1	5180	4.5	61	57	4.0	1.2	–	1.2
6N/7W-23A P1	19.9	6/3/02	4.94	6180	4.9	44	44	0.5	2.0	–	2.0
"Perched" aquifer-lower unit											
6N/7W-23A EM-3	37.7	6/3/02	8.4	562	–	21	20	0.8	3.0	3.0	3.0
6N/7W-23A EM-1	36.7	6/4/02	8.4	812	–	15	14	0.8	3.3	3.2	3.3

[All chromium values dissolved. Cr(T), total chromium (Cr VI + Cr III); Cr VI, hexavalent chromium; Cr III, chromium-III; μS/cm, microsiesmens per centimeter; mg/L, milligrams per liter; mg/L, micrograms per liter; ‰, parts per thousand].

of Cr(III) in water from some on-site wells are consistent with reductive fractionation of Cr(VI) to Cr(III).

An analysis of the changes in Cr(VI) concentrations and $\delta^{53}Cr$ compositions was done to determine the source of Cr and the relative effects of fractionation and mixing on the composition of water from on-site wells. Given the uncertain and complex history of Cr releases at the site the initial Cr concentration and $\delta^{53}Cr$ composition was not precisely known. However, the initial composition is probably bounded by the composition of water from well EM-13 (having the highest Cr concentrations) and water from well EM-16 (having the lowest $\delta^{53}Cr$ composition). Assuming (1) initial Cr concentrations and $\delta^{53}Cr$ compositions in this range and reductive fractionation, the expected range in Cr concentrations and isotopic compositions was calculated using Eqs. (1) and (2), presented earlier. Results of these calculations suggest that in some samples as much as 25 to 50% of the original Cr may have been removed by reductive fractionation (Fig. 14). The extent of reduction may be reasonable in water from well EM-19 where almost 18% of the total dissolved Cr is present as Cr(III). However, reductive fractionation of Cr(VI) to background concentrations would produce $\delta^{53}Cr$ values ranging from 2.3 to 11‰. $\delta^{53}Cr$ values in this range were not present in water from wells at the site.

In previous studies, Ellis et al. (2002) presumed that background Cr(VI) concentrations were low and that all measureable Cr(VI) was the result of anthropogenic releases. As a consequence, the potential for mixing of native water containing Cr(VI) with anthropogenic Cr(VI) was not considered. In contrast to Ellis et al. (2002) work the expected range of Cr concentrations and $\delta^{53}Cr$ values within the plume at this site were calculated by assuming simple mixing of Cr(VI) and $\delta^{53}Cr$ in water from wells EM-16 and EM-13 and background values from wells 27B8 and 24D1. The expected range in concentration and $\delta^{53}Cr$ composition is smaller than the range calculated assuming reductive fractionation of Cr(VI) and does not include water from all wells at the site.

Although both reductive fractionation and mixing probably occur at this site, reductive fractionation provides a better model of the measured data. However, the extent of reductive fractionation is limited at the site.

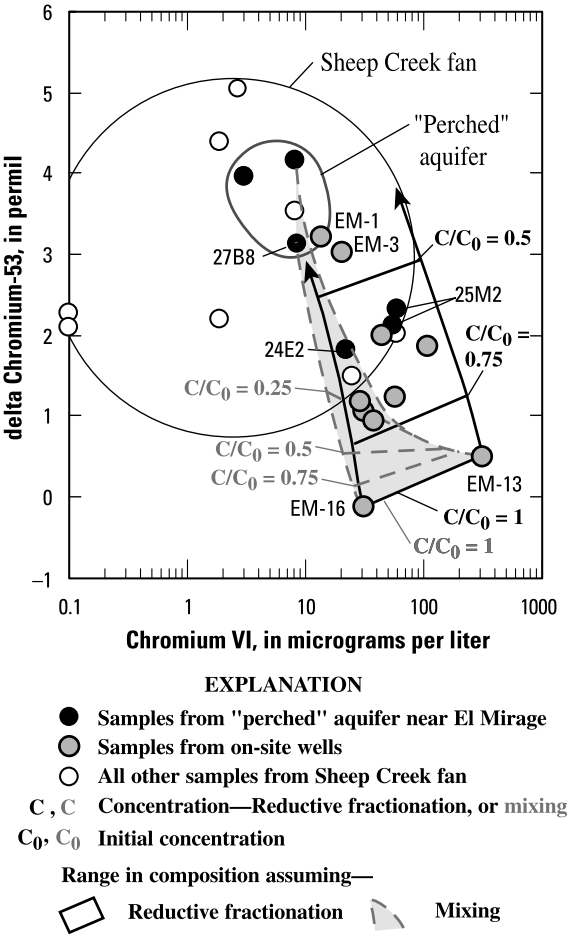

Fig. 14. Chromium(VI) concentrations and the $\delta^{53}Cr$ composition of water from selected wells in the Sheep Creek fan and at an industrial site near El Mirage, western Mojave Desert, southern California.

Water from two domestic wells (6N/7W-24E2 and 25M2) in the perched aquifer have Cr(VI) concentrations of 22.1 and 60 μg/L, and $\delta^{53}Cr$ compositions of 1.8 and 2.3‰, respectively (Table 2). The chemical and isotopic compositions of water from these wells also plot within the region of expected Cr(VI) and $\delta^{53}Cr$ compositions in the perched aquifer (Fig. 10) and within the range of expected Cr(VI) concentrations and $\delta^{53}Cr$ compositions at the site (Fig. 14).

Well 6N/7W-24E2 is adjacent to the site (Fig. 1). Water from well 24E2 has shifts in major-ion composition from increased SO_4^{2-} concentrations similar to that of water from wells at the site (Fig. 12). Fractionation of $\delta^{18}O$ and δD are consistent with partial evaporation prior to recharge that are similar in magnitude to those measured in shallow wells at the site (Fig. 13).

Well 6N/7W-25M2 is about 2 km to the south and is upgradient from the site. Although the major-ion composition of water from well 25M2 is similar to that of the high Cr ground-water at the site (Fig. 12) and the isotopic composition of water from the well also has been fractionated by evaporation (Fig. 13), the magnitude of the fractionation is less than the magnitude measured in wells at the site. Given the location of well 25M2 (upgradient from the site) and the differences in $\delta^{18}O$ and δD composition, it is possible that high Cr(VI) concentrations in water from well 25M2 may have originated from some source other than the chemical milling facility. Water from well 25M2 has NO_3^- in excess of the U.S. Environmental Protection Agency MCL of 10 mg/L as N and is adjacent to irrigated agriculture and dairy operations. It is possible that movement of irrigation-return and dairy wastewater mobilized Cr from the unsaturated zone underlying the Sheep Creek fan. Chromium concentrations in water from well 25M2 are higher than water from most wells in the perched aquifer and in the same range as water from some wells at the chemical milling facility, and mobilization of Cr from the unsaturated zone could contribute some Cr to ground-water underlying that site. However, the very high concentrations in water from some observation wells and the $\delta^{53}Cr$ isotopic compositions near 0‰ are consistent with an anthropogenic source of Cr.

5. Conclusions

Chromium occurs naturally in rock and alluvium in the western Mojave Desert. Chromium concentrations exceeding 1000 ppm were measured in amphiboles, possibly actinolite, within the Pelona Schist in the San Gabriel Mountains. Within the alluvium most of the Cr was in the HCl-extractable fraction and associated with Fe and Mn oxides on the surfaces of mineral grains. When Cr concentrations in the HCl-extractable fraction were normalized for Fe and Mn concentrations in the extract, the Cr saturation on Fe and Mn exchange sites in alluvium eroded from mafic and granitic sources was similar.

Chromium(VI) concentrations in excess of the California Maximum Contaminant Level (MCL) of 50 μg/L occur naturally in alkaline, oxic ground-water in alluvial aquifers in the western Mojave Desert, southern California. The highest concentrations were measured in alluvial aquifers eroded from mafic rock, but Cr(VI) as high as 27 μg/L was measured in aquifers eroded from granitic rock. Chromium concentrations were higher in mafic and alluvial aquifers having pH greater than 7.5 and dissolved O_2 concentrations greater than 0.5 mg/L. Almost all the Cr in water from sampled wells in the study area was present as Cr(VI). In addition to pH and redox, natural Cr concentrations also are controlled by the concentration and saturation of Cr sorbed on Fe and Mn oxides on the surfaces of mineral grains that compose the alluvial aquifers. This partly explains high Cr(VI) concentrations in alluvial aquifers eroded from granitic rock that lack obvious sources of Cr.

Chromium(VI) in ground-water in alluvial aquifers in the western Mojave Desert is fractionated with respect to the average $\delta^{53}Cr$ of the earth's crust and with respect to the $\delta^{53}Cr$ composition of rock and Cr-containing minerals in the study area. The $\delta^{53}Cr$ composition in ground-water is a complex function of the combined rate of mineral weathering, oxidation, exchange with Cr sorbed on mineral grains and a function of the rate of Cr(VI) reduction to Cr(III) (Table 4). Data presented in this paper suggest that mineral weathering, oxidation and reduction of Cr sorbed on mineral grains, and subsequent exchange releases Cr to solution having a $\delta^{53}Cr$ composition greater than 0‰. As dissolved O_2 is consumed, reduction of Cr(VI) to Cr(III) and subsequent precipitation of Cr(III) removes the lighter isotopes, further increasing the $\delta^{53}Cr$ composition of the Cr remaining in solution.

Anthropogenic Cr released to the environment from industrial activity has a Cr isotopic composition of 0‰. If background $\delta^{53}Cr$ compositions in native ground-water from a given area are known, then the extent of Cr(VI) anthropogenic can be determined—even in areas having high background Cr(VI) concentrations. Care must be used in interpretation of data from contaminated sites because reduction of Cr(VI) to Cr(III) within plumes can produce positive (heavier) $\delta^{53}Cr$ compositions that overlap the range in native ground-water. In such cases it may still be possible to use $\delta^{53}Cr$ compositions in conjunction with hydraulic, major-ion, or $\delta^{18}O$ and δD data to determine the extent of Cr contamination. Perhaps the greatest benefit of Cr isotopes in contaminant studies will ultimately be in understanding processes that occur within Cr plumes. In areas where Cr isoto-

Table 4
Simplified chromium chemistry and $\delta^{53}Cr$ isotopic systematics in alkaline, oxic alluvial aquifers, western Mojave Desert, USA

Process	Location	Water Chemistry	Isotopic fractionation
Weathering of Cr(III) from primary minerals	Soils in mountain uplands	Oxic, neutral pH, Cr(III) insoluble	None
Oxidation of Cr(III) to Cr(VI) by manganese oxides	Surface of mineral grains	Oxic, neutral pH, Cr(III) and Cr(VI) insoluble	Negligible
Reduction of Cr(VI) to Cr(III) by reduced iron, organic carbon, or other natural reductants	Surface of mineral grains	Oxic, neutral pH, Cr(III) and Cr(VI) insoluble	Lighter isotopes preferentially reduced to Cr(III), heavier isotopes, preferentially remain as Cr(VI). Total chromium isotopic composition (Cr(III) plus Cr(VI)) sorbed on solid phase near 0‰
Exchange of Cr(VI) into solution	From solid to solution	Oxic, alkaline pH (>7.5). Increases in pH driven by silicate weathering. Cr(III) insoluble, Cr(VI) soluble	None. Heavier isotopes in Cr(VI) enter solution Isotopic composition in solution independent of Cr(VI) concentration. Lighter isotopes in Cr(III) remain sorbed on solid phase. Effective isotopic composition sorbed on solid phase may remain near 0‰ if the mass of chromium sorbed on the solid greatly exceeds the mass in solution
Reduction of Cr(VI)	From solution to solid. In deeper parts of alluvial aquifers and at the down gradient end of long flow paths	Suboxic to reducing (dissolved oxygen <0.5 mg.L). Dissolved oxygen consumed by organic carbon and other reductants along flow path through aquifers. Cr(III) insoluble, Cr(VI) insoluble	Heavier isotopes preferentially remain in solution Lighter isotopes preferentially reduced to Cr(III) and removed from solution. Process continues as dissolved oxygen is consumed, all Cr(VI) is reduced to Cr(III) and removed from solution

>, greater than; <, less than.

pic data suggest rapid reduction of Cr(VI) to Cr(III), natural remediation and monitoring may be suitable management options to control plume migration. In other areas where Cr isotopic data suggest slow reduction of Cr(VI) to Cr(III) and mixing processes predominate, more aggressive management activities such as pump-and-treat or in situ remediation may be required to control plume migration.

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