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Geologic Origin and Pathways of Selenium from the California Coast Ranges to the West-Central San Joaquin Valley

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I. INTRODUCTION

Contamination at Kesterson Reservoir led to the assessment of a naturally occurring, potentially toxic, trace element, selenium (Se), from source geologic formations in the surrounding California Coast Ranges. Selenium has been mobilized and concentrated by weathering and evaporation in the process of soil formation and alluvial fan deposition in the arid and semiarid climate of the west-central San Joaquin Valley. This deposition has created a soil salinization problem, and impeding alluvial clay layers have led to waterlogged soils as lands have been reclaimed by flooding to remove the salt and then have been continued to be irrigated. Through current practices of agricultural wastewater management in the valley, subsurface drains are used to collect the saline, shallow groundwater threatening the crop root zone. This wastewater is essentially a soil leachate that was transferred to and stored in wetland areas. This in turn led to extended ecological community exposure to toxic levels of Se and consequent bird deaths and deformities [1].

The contaminant Se was leached from the salinized soils of the extensive alluvial fans developed by Panoche and Cantua Creeks (Figure 1). The highest concentrations of Se (maximum 4.5 $\mu\text{g/g}$, median 1.8 $\mu\text{g/g}$) and sulfur in soils [2] and the highest degree of soil salinization occurred in an interfan area between the two creeks. Ephemeral streams and debris flows

Chapter 6

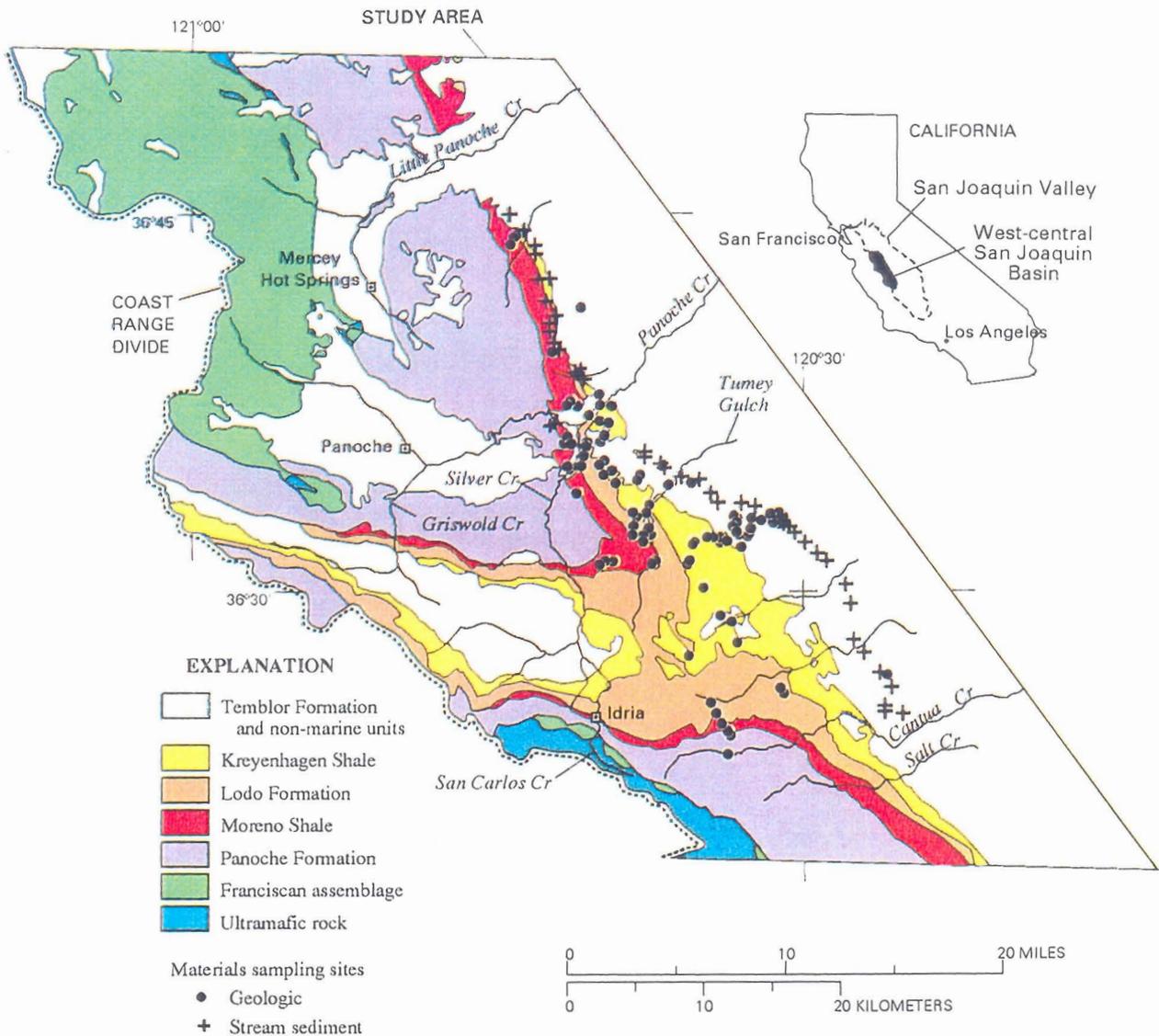


Figure 1 Surficial geology and areal distribution of sampling sites for geologic materials in the study area. (Compiled from Refs. 9 and 16–19 by the Geographic Information Service of the U.S. Geological Survey.)

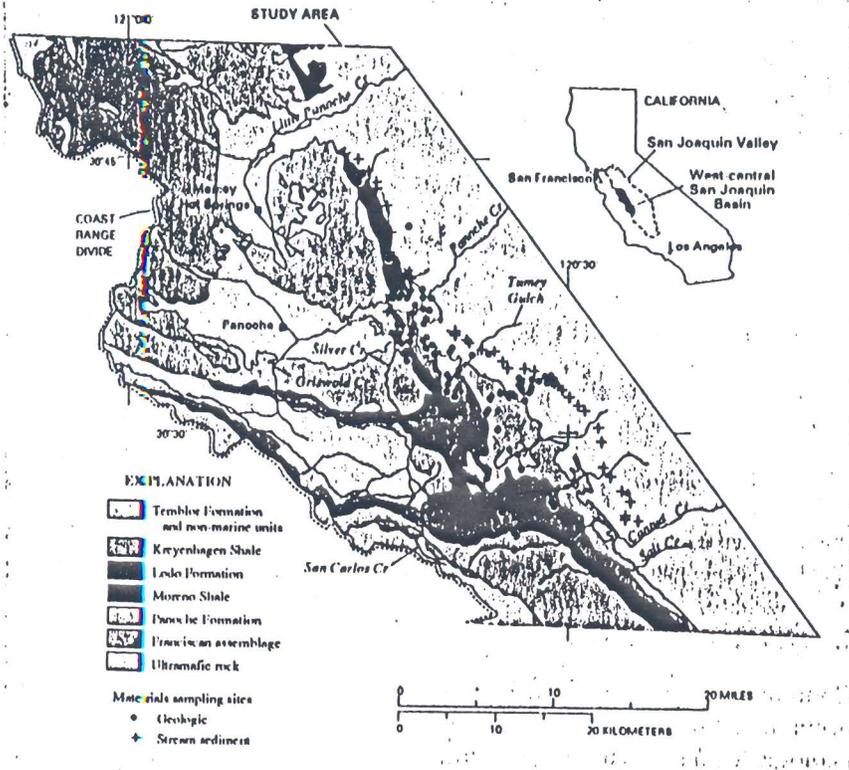


Figure 1 Surficial geology and areal distribution of sampling sites for geologic materials in the study area. (Compiled from Refs. 9 and 16–19 by the Geographic Information Service of the U.S. Geological Survey.) (See color plate.)

that rarely reach the valley axis terminate in this interfan area and develop the most elevated concentrations of Se, as in a closed basin. The highest concentrations of Se in shallow groundwater occur in the same area and along the adjacent southern distal end of the Panoche Creek fan [3]. Selenium concentrations in soils do not follow creek drainages like those of arsenic and mercury, which are deposited at the base of the creeks on the fans and remain there, suggesting that the majority of Se is mobilized in a soluble form. This Se then may be carried by the streams or leached out of the alluvial fans to ultimately reach the San Joaquin River trough, if not intercepted by subsurface drains. Soluble Se and salts continually

concentrate at the toes of the alluvial fans through downslope movement and evapotranspiration and move into the shallow groundwater as the valley floor is irrigated. Recharge at fan heads also contributes to Se in shallow groundwater [4]. The shallow groundwater aquifer, once thought to be a series of perched aquifers, is continuous [5] and extends in this area to depths of 120–240 m below land surface [6].

Tracing of sulfate, selenate, and sodium, which were significantly correlated ($r = 0.93$ for Se and sulfate; $r = 0.99$ for sodium and sulfate) in the subsurface agricultural drainage [7], eventually led to the consideration of marine, pyritic (FeS_2) sedimentary rocks in the Coast Ranges as the possible geologic source. This type of rock could provide the abundant, soluble sodium and magnesium sulfate minerals creating the soil salinization of the valley. Berner [8] considers pyrite to be the main source of sulfate in marine shales formed from the reduction of sulfate-containing pore waters during diagenesis. Upon weathering, this sulfur is again oxidized to sulfate and can be moved in aqueous systems, appearing as efflorescences or evaporites in arid climates. Preliminary sampling of Panoche, Silver (a major tributary to Panoche Creek), and Cantua Creeks showed sodium-magnesium-sulfate waters with low concentrations of Se ($<10 \mu\text{g/L}$) [9].

From the geologic record, Se contamination has been proposed to result from the dissolved mineral load ultimately drained from seleniferous Cretaceous marine sedimentary strata underlying and surrounding basins such as the San Joaquin Valley [10]. Extensive volcanic eruptions during Cretaceous time are thought to be the primary source of Se through deposition in Cretaceous seas that had invaded a considerable part of the western states [11]. Selenium was either eroded from igneous rocks or became incorporated in rainfall from volcanic gases and dust in the atmosphere. In either case, Se was incorporated in sediments that have been uplifted over time and exposed to weathering and erosion. Shales commonly contain more Se than other sedimentary rocks [12]. Historically, analytical data from the Cretaceous marine Pierre and Niobrara Shales have shown the highest concentrations of Se (maximum, $103 \mu\text{g/g}$; median $6.5 \mu\text{g/g}$) in the western United States [13]. Plants grown on soils derived from these shales were found to be toxic to range animals [13]. More recently, reconnaissance of refuge areas in the western United States has shown significant Se contamination [14].

This chapter investigates the water quality of seeps, springs, and streams and characterizes evaporative salts, bedrock (geologic materials), soils, and stream sediments in the areas contributing to the Panoche and Cantua Creek alluvial fans. The principal geologic formations have been

identified, and a conceptual model has been developed that explains the predominant mobilization and transport processes. The model accounts for the spatial and temporal variations in Se concentrations.

II. METHODS

Methods of collection, preservation, and elemental analysis of water samples were adapted for saline geochemical environments and are given in Presser and Barnes [7]. The analytical scheme for analysis and speciation of Se in water and salt samples is given by the same authors in Ref. 15. Sampling and analysis methods of geologic materials are given in Presser et al. [9]. All of the analyses for Se used hydride generation atomic absorption spectrophotometry. Care must be taken in pretreatment steps for this method to ensure that all the different forms of Se are available for signal generation [15]. Minerals were identified by X-ray diffraction; analysis was difficult because of the transient nature of some of the hydrated salts.

III. STUDY AREA AND GEOLOGIC SETTING

Alluvial deposits of the west-central San Joaquin Valley are derived primarily from the eastern side of the Coast Ranges. The study area is in the part of the eastern Coast Ranges between Panoche and Cantua Creeks. It encompasses 2600 km² (1000 sq m) and 11 drainage basins, from the drainage divide in the west to the alluvial fans in the east and from Salt Creek in the south to Little Panoche Creek in the north. Geologic formations of significant extent in the study area [16–19] are listed in Table 1 and shown in Figure 1.

The Coast Ranges evolved from complex folding and faulting of sedimentary and igneous rocks of Mesozoic and Tertiary age. Major deformation began in Miocene time and continued at intervals through the Pleistocene, when the mountains were raised to their present heights of 1200–1500 m [20].

A simplified structural model of central and northern California Coast Ranges is given by Irwin and Barnes [21]. It shows the Salinian block along the west side of the San Andreas fault and the Franciscan assemblage and Great Valley sequence along the east side. The Great Valley sequence consists of the marine Upper Cretaceous Panoche Formation and the Upper Cretaceous-Paleocene Moreno Shale. The Coast Range thrust fault is the regional contact between the Franciscan assemblage (lower plate) and serpentinite at the base of the Great Valley sequence (upper plate). A thick sequence of Tertiary marine and nonmarine sediments and some

Table 1 Sampled Geologic Units of the California Coast Ranges Study Area

Age	Type	Formation	Water type
Quaternary	Nonmarine sediments	Older alluvium and terrace deposits	Dilute Na-Cl, HCO ₃
Pliocene to Pleistocene	Nonmarine sediments	Tulare Formation	Dilute Na-Cl, HCO ₃
Miocene (?)	Ores	Mineralization of the New Idria Mercury Mining District	Fe, Mg-SO ₄ acid mine drainage
Eocene to Oligocene	Marine sediments	Kreyenhagen Shale (includes Tumey Formation)	Saline Na, Mg-SO ₄
Eocene	Marine sediments	Domengine Formation	Saline Na, Mg-SO ₄
Paleocene to Eocene	Marine sediments	Lodo Formation	Saline Na, Mg-SO ₄
Late Cretaceous to Paleocene	Marine sediments	Moreno Shale	Saline Na, Mg-SO ₄
Late Cretaceous	Marine sediments	Panoche Formation	Saline chloride
Late Jurassic to Late Cretaceous	Meta-sedimentary	Franciscan assemblage	Bicarbonate
Jurassic	Intrusive	Ultramafics, mainly serpentinitized	Mg ultrabasic

Source: Compiled from Ref. 9.

volcanic rocks locally overlie the region. Tectonic piercement of the Great Valley nappe by the underlying Franciscan rocks occurs at Mt. Diablo and New Idria. In the northern Coast Ranges, most of the nappe has been removed by erosion, so the structurally lower Franciscan rocks are exposed over a wide area. The New Idria piercement structure is a prominent feature in the area of the Coast Ranges implicated to be the source of selenium contamination at Kesterson Reservoir. Acid mine drainage from the New Idria Mining District [22] discharges into Panoche Creek via Silver Creek. The district consists of about 20 quicksilver deposits that rim a fault-bounded core of serpentinite and Franciscan rocks that have been extruded through beds of Upper Cretaceous Panoche Formation. The most productive mercury deposits are found in hydrothermally altered and fractured Panoche Formation along the perimeter of the core.

IV. TYPES OF FLUIDS OF THE COAST RANGES FORMATIONS

Characteristic fluids issue from the principal tectonic blocks just described. Those encountered and sampled in the study area during a survey of creeks, springs, and seeps, which encompassed 62 hydrologic sample sites [9], yielded the following information on dissolved mineral type:

1. Sodium- and magnesium-sulfate waters were derived from Upper Cretaceous and Tertiary marine sedimentary rocks, including the Moreno and Kreyenhagen Shales and the Lodo Formation.
2. Chloride waters were derived from the marine Upper Cretaceous Panoche Formation (part of the Great Valley sequence) and a zone of hydrothermal alteration at Mercey Hot Springs.
3. Bicarbonate waters were derived from the Franciscan assemblage.
4. Ultrabasic, high-magnesium waters were derived from serpentinites.
5. Iron-magnesium-sulfate acid mine drainage was derived from the New Idria Mercury Mining District.

Only the sodium- and magnesium-sulfate waters contained concentrations of Se greater than 3 µg/L. In previous discussions of Coast Ranges geohydrology, sulfate waters have been largely ignored.

To help determine the source of these waters, isotopic compositions of $\delta^{18}\text{O}/^{16}\text{O}$ and $\delta \text{D}/\text{H}$ for all the spatially and chemically divergent groundwater and surface water samples were analyzed [9]. These data fall on an evaporative trend line with a correlation coefficient of 0.93, indicating a single source for the waters. This isotopic limitation suggests that the solute chemistry of the fluids is controlled and/or modified by solution-precipitation processes of surficial and subsurface evaporites rather than by mixing of distinct water sources.

V. EVALUATION OF GEOLOGIC SOURCES OF SELENIUM

A. Concentrations in Bedrock

Cretaceous and Tertiary marine sediments dominate the Coast Ranges study area, which drains to the west-central San Joaquin Valley. These marine shales and sandstones weather into a sulfate regime evidenced by extensive surficial salt efflorescences and evaporites at water and shale surfaces. It is along this eastern flank of the Coast Ranges that a survey of bedrock and stream sediment samples was taken (Figure 1). The Monocline Ridge area is immediately above the interfan area that contains

the highest degree of Se contamination. Geologically, it is a massive exposure of the Kreyenhagen Shale shown in yellow in Figure 1.

To determine sources of Se in the study area, 117 bedrock samples were collected in 1986 (Figure 1) [9]. The marine Upper Cretaceous-Paleocene Moreno Shale and the Eocene-Oligocene Kreyenhagen Shale (Figure 1) contain elevated levels of Se, with a maximum of 45 ppm and medians of 6.5 and 8.7 ppm, respectively. Selenium concentrations of these shales are compared with the medians (Figure 2) of other formations in the area (Figure 1): the Upper Cretaceous Panoche Formation, 1.0 ppm; the Paleocene-Eocene Lodo Formation, 0.8 ppm; the Pliocene-Pleistocene Tulare Formation, 1.2 ppm; and Quaternary nonmarine sediments, 0.7 ppm. The Panoche Formation is mainly sandstone, and the Lodo Formation, within this study area, is mostly sandstone. Few samples were collected in the Panoche Formation because of the poor exposure of the shale facies and the presence of nonseleniferous chloride waters. The other geologic units were evaluated only through the characteristic water chemistries associated with them, which were not indicative of probable Se enrichments.

B. Lithology of Seleniferous Shales

1. Upper Cretaceous to Paleocene

MORENO SHALE (MARINE) Foraminiferal and diatomaceous chocolate-brown to maroon, platy, friable shales; lower part contains numerous beds of sandstones with concretions and dikes; upper part is more nearly pure shale and contains a greater proportion of material of organic origin; forms extensive colluvial slopes [23]. Near Cretaceous-Tertiary boundary, planktonic and benthic foraminifera generally indicate a submarine slope and associated basinal depositional facies [24]. Type locality is Moreno Gulch; part of Great Valley sequence. Thickness: 300-900 m.

2. Eocene and Oligocene

KREYENHAGEN SHALE (MARINE) Thin-bedded, chocolate-brown shale and mudstone, grading upward to diatomaceous shale and diatomite; lithic sandstone in lower part; lens of gray lithic sandstone containing prominent oyster beds in upper part along Monocline Ridge [25]. On the basis of Eocene planktonic and benthic foraminifera and calcareous nannoplankton, deposition was in a submarine slope environment [26]. Includes the Tumey Formation because of lithological similarity [27]. Thickness: 450 m.

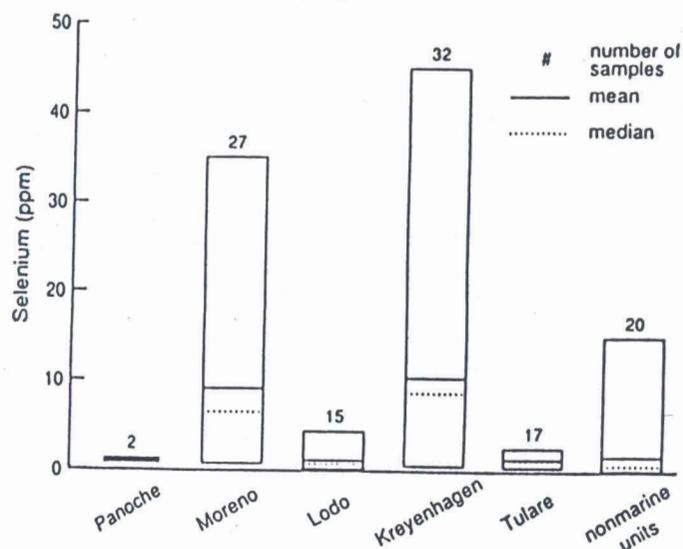


Figure 2 Number of samples, means, medians, and ranges of selenium concentrations in geologic samples by formation. (Modified from Ref. 9.)

VI. MOBILIZATION MECHANISMS

A. Dissolution of Salts and Dissolved Mineral Load

Chemistry of streams and seeps of the drainage basins in the study area is controlled by sodium and magnesium sulfates. The waters are characterized by high dissolved solids (up to 421,400 mg/L). The highest concentration of sodium is 44,000 mg/L; of magnesium, 56,000 mg/L; and of sulfate, 318,000 mg/L.

Thirteen predominantly hydrous, sodium magnesium sulfate minerals (Table 2), visible as extensive surficial efflorescences at water/shale interfaces, were identified in the Coast Ranges study area. The salts contain elevated levels of Se as selenate up to 25 ppm [9]. These sulfate minerals also contain up to 10 waters of hydration and consequently increase in volume by as much as 29% from the dehydrated state. Theoretically, these loose, open-lattice structures of the hydrous minerals could incorporate the selenate (SeO_4^{2-}) anion in the sulfate (SO_4^{2-}) space. These minerals can therefore act as temporary geologic sinks for Se. Samples of the mixed sodium and calcium hydrated mineral hydroglauberite contain up to 14 ppm Se, but samples of gypsum contain <0.5 ppm Se. These results

Table 2 Efflorescent Sulfate Minerals Containing Elevated Selenium in the California Coast Ranges Study Area

Name	Formula
Mirabilite	$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
Thenardite	Na_2SO_4
Bloedite	$\text{MgNa}_2(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$
Konyaite	$\text{MgNa}_2(\text{SO}_4)_2 \cdot 5 \text{H}_2\text{O}$
Loeweite	$\text{MgNa}_2(\text{SO}_4)_2 \cdot 2\frac{1}{2} \text{H}_2\text{O}$
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Starkeyite	$\text{MgSO}_4 \cdot 4 \text{H}_2\text{O}$
Pentahydrate	$\text{MgSO}_4 \cdot 5 \text{H}_2\text{O}$
Hexahydrate	$\text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$
Epsomite	$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$
Ferrohexahydrate	$\text{FeSO}_4 \cdot 6 \text{H}_2\text{O}$
Hydroglauberite	$\text{Na}_{10}\text{Ca}_3(\text{SO}_4)_8 \cdot 6 \text{H}_2\text{O}$
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$

Source: Modified from Ref. 31 with permission.

indicate an exclusion of Se from gypsum and a concentrating mechanism for Se in the more soluble sulfate salts. A majority of halite, as opposed to sulfate salts, was found in the Panoche Formation, which also contains <0.5 ppm Se.

Efflorescent salt crusts on exposed source shales are enriched up to sevenfold in Se compared with their substrates. These deeply weathered shales at higher elevations can contain 95% of the total Se as soluble selenate. In typical hillslopes developed on the Moreno and Kreyenhagen Shales, evaporation from the capillary fringe on summit slopes and salt layering from downgradient throughflow on toeslopes concentrates Se in these slope positions (median values of 12 and 8.2 ppm, respectively) relative to the midslope position (median 4.4 ppm). Therefore, subsurface water movement and fractional crystallization appear to effectively redistribute soluble Se.

B. Weathering of Pyritic Shale Evidence

These sulfate minerals show that the chemistry of the weathering of reduced shale (oxidation of pyrite) is largely a reversal of the chemistry of the early diagenesis of the shale (reduction of sulfate) [8]. Because of

similar chemical and physical properties, Se substitutes for sulfur in pyrite (FeS_2) in sedimentary rock at concentrations up to 300 ppm [28]. Up to 3% Se has been found in surveys of Colorado Plateau deposits along with ferroselite (FeSe_2), the Se analog of pyrite [29]. The presence of acidic (pH 4) sodium- and magnesium-sulfate seeps gives evidence in the study area for the acid-producing reaction of the weathering of pyrite [30] and, by inference, ferroselite. Five examples of these seeps with elevated levels of Se, up to 420 $\mu\text{g Se/L}$, were found in widely separated areas of the Moreno Shale [31]. Water chemistries of two of these seeps, at Tumey Gulch and Arroyo Hondo, are given in Table 3. Besides elevated Se, these acid waters contain high levels of dissolved metals; maximum concentrations are 188 mg/L aluminum, 95 mg/L manganese, 13 mg/L zinc, 9 mg/L nickel, and 1.7 mg/L cobalt.

Neutralization and evaporative concentration of these waters and fractional crystallization of sulfate minerals result in a near-surface sodium-sulfate fluid that exceeds the USEPA limit for a toxic Se waste (1000 $\mu\text{g/L}$). These processes occur in an ephemeral stream at the Tumey Gulch site directly above the interfan zone containing the maximum Se concentrations in soils on the valley floor. The alkaline ephemeral stream (Table 3) from this drainage rarely reaches the valley floor, making this a mainly closed evaporative basin. The alkaline site is geologically similar to the acid site, all being dominated by the Moreno Shale, but the stream water is strongly buffered by bicarbonate water (pH 8.6 and 1415 mg/L HCO_3) derived from the Lodo Formation. As this water is neutralized by adjacent alkaline carbonates, heavy metals are precipitated out (<0.3 mg/L aluminum, 1 mg/L manganese, <0.1 mg/L zinc, 0.6 mg/L nickel, <0.1 mg/L cobalt). The Eh-pH diagram for Se [13], however, shows that neutralization aids the oxidation of Se to soluble selenate, thus mobilizing the Se up to 3500 $\mu\text{g/L}$. This oxidation would not have taken place in an acid environment, where it is known that insoluble iron-selenite compounds containing 12 ppm Se can exist under an annual rainfall of 100 in. [13]. The alkaline ephemeral stream water is also 2 M in sodium sulfate salt and precipitates mirabilite upon standing. However, analysis of the reaction states of the aqueous solution with respect to various minerals, using the chemical equilibrium computer program SOLMNEQ [32], shows that the water is undersaturated with mirabilite. Theoretically, this could indicate impure crystal growth or slightly inaccurate data on either thermochemical solubility or aqueous species complexation. If this undersaturation represents equilibrium, then similar results for some of the pH 4 series of waters suggest that the Se content of both of these types of waters could be controlled by mirabilite (or an equally soluble magnesium or mixed

Table 3 Selenium Concentrations and Water Chemistry of Acid and Alkaline Seleniferous Waters^a

	Se ($\mu\text{g/L}$)	Water type	Water components (mg/L)											pH		
			TDS ^b	Na	SO_4	K	Mg	Ca	H ^c	HCO_3 ^d	Cl	SiO_2	B			
Acid Waters																
Acid seeps in Moreno Shale																
1	420	Na-SO ₄	18,000	3,850	12,500	50	895	395	10			150	61	8.0	4.40	
2	195	Na-SO ₄	50,000	9,850	34,500	35	3700	470	16			1,100	89	13.	3.85	
Alkaline Waters																
Ephemeral stream																
3	3500	Na-SO ₄	160,000	44,000	88,000	200	7550	635				1400	18,200	67.	8.55	
Runoff																
4 ^e	55	NaMgCa-SO ₄	6,200	845	3,700	19	300	475				205	95	3.0	7.8	
Panoche Road																
5 ^e	57	NaCaMg-SO ₄	3,700	495	2,400	17	170	410				150	125	2.0	7.9	
highway I-5																
6	18	NaMg-SO ₄	6,500	1,000	3,950	15	490	275				525	240	12	10.	8.20
Moreno landslide																
Integrated watershed																
7	140	NaMg-SO ₄	3,600	575	1,900	6	245	160				555	80	26	5.5	7.70
waters seep I																
8	155	Na-SO ₄	4,350	920	2,350	7	145	185				440	250	6	9.7	7.95
headwaters																
Well																
9	56	CaMgNa-SO ₄	3,000	295	1,650	4	195	360				220	270	38	4.0	7.20
domestic at 400 ft																

^aData are reported in significant figures (2-5 maximum).

^bTotal dissolved solids.

^cTotal acidity as H.

^dTotal alkalinity as HCO_3 .

^eCalifornia Department of Water Resources data except for Se.

Source: Modified from Ref. 31 with permission.

sodium and magnesium sulfate). Selenate in solid solution with the soluble sulfate phase could then hypothetically determine the Se concentration in the waters.

VII. TRANSPORT MECHANISMS

A. Waters

Transport waters representative of Se mobilized by these processes indicate a significant hydrologic reservoir of Se (Table 3) [9]. Runoff from winter flushing events from the two major drainages, Silver and Panoche Creeks, near the valley floor contains approximately 60 $\mu\text{g Se/L}$. The $\delta^{18}\text{O}/^{16}\text{O}$ and $\delta\text{D/H}$ analyses of surface water samples collected at higher elevations 12 days into the storm hydrograph remained on the isotopic evaporative trend line for prerafall samples. Concentrations of Se (up to 19 $\mu\text{g/L}$) also remained elevated in these waters, providing evidence for the importance of subsurface flow in making Se available for transport. Samples of perennial groundwater associated with structural synclines at the heads of Griswold and Silver Creeks (Figure 1), in the upper reaches of the Panoche Creek drainage, represent integrated waters encompassing the geologic section from Jurassic to Miocene. These waters contain elevated Se at an average concentration of 148 $\mu\text{g Se/L}$. Water samples from deeper wells (120 m) in Panoche Valley contain up to 56 $\mu\text{g Se/L}$.

B. Mass Wasting and Suspended Sediment

The steeply dipping marine shales, especially the Moreno Shale, show characteristic instability [33], which leads to extensive mud and debris flows, slumps, piping, and deeply incised gullies. Low effective rainfall (25–35 cm/yr) supports little vegetation on steep, poorly consolidated slopes, which allows severe erosion in the higher hills and produces rapid alluvial fan deposition below [34]. Selenium concentrations of bed sediments in ephemeral drainages in Moreno Shale-derived materials range from 3.6 to 8.5 ppm Se, with a median of 6.8 ppm.

Data from analysis of 48 sediment samples from ephemeral streams emerging from the foothills near the point of discharge onto the alluvial fans [9] (Figure 1) show a median of 0.8 ppm Se downslope from the Kreyenhagen Shale and 2.8 ppm Se downslope from the Moreno Shale. The sediments from the Moreno Shale were observed to include recent, more localized, debris-flow materials. A survey of 21 channel sediment samples in a longitudinal profile of the main drainage of the study area (San Carlos, Silver, lower Panoche Creeks, Figure 1) shows a uniform

background of 1–2 ppm Se regardless of adjacent formations. This survey includes an iron hydroxide mat (<0.5 ppm Se) deposited in San Carlos Creek downstream from a tailings pond of the New Idria Mercury Mining District. A second profile after a rainfall event shows a range of 1.7–2.9 ppm Se, with a median of 2.4 ppm. In the final deposition stage of the Panoche Creek system, before issuance onto the alluvial fan, the fine-grained residual deposit of suspended load contains 95% of the low-level Se in the insoluble fraction.

VIII. SUMMARY AND MODEL

The irrigated farmlands giving rise to the most contaminated shallow groundwater collected as subsurface drainage and delivered to Kesterson NWR lie just downslope of the interfan area between Panoche and Cantua Creek alluvial fans and at the southern distal end of the Panoche Creek fan. This is where Se and sulfur in soils and soil salinities were highest in 1984. A reconnaissance of the rock outcroppings in the drainage basins to this area from the surrounding Coast Ranges showed elevated concentrations of Se in the extensive surficial exposures of the marine Upper Cretaceous-Paleocene Moreno and Eocene-Oligocene Kreyenhagen Shales. These shales have decreasing exposures to the north and to the south. Alternative source materials investigated in the California Coast Ranges, including Cretaceous and Tertiary sandstones, Pliocene-Pleistocene continental rocks, and waters from the Franciscan assemblage, serpentinites, and the New Idria Mercury Mining District, are comparatively barren of Se.

The occurrence of sodium-magnesium-sulfate waters and minerals associated with the seleniferous rocks and the significant correlation of Se, sulfur, and salinity in alluvial fan soils and of sodium, sulfate, and Se in the inflow waters to Kesterson NWR, led to the proposal that reduced Se in elevated concentrations in these marine pyritic shales is weathered (oxidized) with sulfur, concentrated by evaporation in soluble sulfate (SO_4^{2-}) salts on farmland soils, and mobilized as selenate (SeO_4^{2-}) by irrigation into subsurface agricultural drains.

Within these source formations, two mechanisms are inferred for overall Se transport from the Coast Ranges to the San Joaquin Valley. In the first mechanism, Se moves in solution load, delivering selenate in pulses or episodes of surface runoff. This movement occurs as a result of both rainfall-induced groundwater throughflow and stripping of soluble salts from surface exposures or recently deposited materials during hydrologic events. The arid climate promotes accumulation through many

evaporative concentration-dissolution cycles on semiarid, mass-wasted slopes. This system, consequently, acts as almost a closed basin, open only intermittently during large storms, in developing the elevated Se levels delivered to the fans and, especially, the interfans. Because samples of deeply weathered shales contain 95% of the Se as soluble selenate, mass wasting of accumulated salts may also result in the transport of soluble Se.

Integral to the second mechanism is extensive mass wasting in the form of landslides, slumps, or mudflows, which causes mechanical disintegration of the parent geologic materials that then can be carried and deposited during hydrologic events. Both this material and that eroded from channel banks and beds can transport insoluble Se compounds downstream. These particulate Se compounds may be primary selenides or secondary elemental Se and selenite complexes generated during intermediate weathering. Insoluble forms also may be produced if selenate comes into contact with anoxic environments and is re-reduced. Selenium is not concentrated in stream sediments but rather is lost as it is weathered into the soluble fraction and is washed out. Hence, the Se concentrations associated with stream sediment movement are consistent with those measured in soils on the valley floor [2], and these insoluble species provide a comparatively low-level, solid source concentration of Se, although of large mass, to the alluvial fans. Once dispersed on the fans, this relict form of Se is then oxidized or leached out over time, providing a continuing background of soluble Se contamination to the valley.

IX. CONCLUDING PERSPECTIVES

As suggested by lithological information, the Se-enriched Upper Cretaceous-Paleocene Moreno and Eocene-Oligocene Kreyenhagen Shales are similar in depositional environment, that is, in areas of the continental shelf edge and adjacent continental slopes. These areas are often associated with marine upwellings of nutrient-rich water that lead to periodic plankton blooms. The Miocene Monterey Formation, of similar biogenic nature, is not present in the study area but is a suspected source of Se in the Tulare Lake Bed Area evaporation ponds, further south in the San Joaquin Valley, where deformed birds are now found [35]. Recent studies show values of Se concentrations in the Monterey Formation comparable to those in the Moreno and Kreyenhagen Shales [36].

If this nutrient-rich water is subjected to occasions when there is limited access to the ocean, conditions of anaerobic stagnation may evolve. "Black shales" (i.e., reduced shales rich in organic matter and sulfides, especially pyrite) that contain an enrichment of trace elements, including

Se, greater than that which is normally found in seawater, could form [37,38]. Accumulations similar to those of other bioreactive elements (such as chromium and vanadium) may occur as organic material settles to the sea floor bottom and concentrates these elements in the oxygen minimum zone [39]. The refuge ponds may function as modern analogs of ancient marine seas in which elevated concentrations of Se were known to be deposited in reduced bottom sediments. From such a present-day environment, however, high concentrations of Se are hypothesized to be mobilized and bioaccumulated in the food chain, thus causing aquatic bird deformities.

The correlation of Se and sulfur in the waters derived from the postulated source Cretaceous marine shales led to certain relations being observed. These relations represent a penecontemporaneous occurrence; however, a cogenetic relation has not been proven. It has been generalized that deposits of sulfur-containing minerals are often geochemically secondary, and Se in them could have been redeposited from other sources. Biogeochemically enriched shales, rather than just volcanically enriched Cretaceous shales, are apparently potential source areas [39]. Though not all primary associations of Se have been investigated in this reconnaissance study, the direct interconnection between geologic and ecologic cycles in the San Joaquin Valley through the extensive mobilization of Se from a disseminated source is evident.

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