

**RADIOGENIC ISOTOPE INVESTIGATION OF SOURCES, TRANSPORT, AND  
DEPOSITION OF RARE EARTH ELEMENTS IN THE OWENS LAKE DRAINAGE  
BASIN, EASTERN CALIFORNIA**

by

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Joseph Mario Minervini, M.S.

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Owens Lake is situated in a mostly-closed basin fed by water and sediments derived primarily from the eastern Sierra Nevada range. Radiogenic isotope variations in USGS Owens Lake core OL-92 were used in conjunction with major and trace element concentrations in streams draining the eastern Sierras to investigate sediment provenance, the chemical weathering and transport of rare earth elements (REE) in the Owens Lake drainage basin, and possible climate-related shifts in weathering patterns of the eastern Sierras during the last ~30 ka. Filtered (<0.45  $\mu\text{m}$ ) stream water samples not influenced by hydrothermal fluids or agriculture fall below world average-normalized values for major cations. Concentrations of Nd in the stream water samples are less than  $1 \text{ nmol L}^{-1}$ , too dilute for isotopic analysis. Strontium and neodymium isotopic analyses were conducted on the carbonate and silicate fractions of sediment samples representing deposition in Owens Lake from ~30 ka to ~10 ka. The fraction of carbonate in Owens Lake sediments increases from ~7 to 67 % during this period, reflecting the desiccation of the lake. Strontium, samarium, and neodymium are strongly partitioned into Owens Lake chemical sediments. Over the past ~30 ka,  $\epsilon_{\text{Nd}}$  values of clastic sediments in Owens Lake remain relatively constant, near -6.5. Chemical sediments remain approximately one epsilon unit higher than the clastic sediments until ~12 ka ago, at which time they shift to less radiogenic values, matching those of the clastic sediment. Differential mineral weathering of

more common mineral phases over REE-enriched accessory phases is the most likely cause of the isotopic shift in Owens Lake chemical sediments at ~12 ka ago. Preferential weathering of hornblende could displace the Nd isotopic composition of Owens Lake chemical sediments away from that of the clastic fraction. Depletion of hornblende could allow the Nd isotopic composition of the two sediment fractions to return to similar values. This study represents the first Nd isotope study of a lacustrine system and suggests Nd isotopes could be a useful paleoclimate proxy. Additional work in older Owens Lake sediments and in other lake systems is clearly warranted.

## **FOREWORD**

This thesis is dedicated to my parents in appreciation of a lifetime of support, guidance, love, and friendship. Special thanks to Brian K. Games for countless hours of assistance with laboratory instruments and procedures, and to John R. Boulanger for assistance with the collection of field data. Finally, I thank my thesis committee, Drs. Brian W. Stewart, Rosemary C. Capo, and William P. Harbert, for their patience, guidance, support, and for providing this soil scientist the opportunity to study geology.

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## 1. INTRODUCTION

Processes governing the origin and nature of chemical and clastic sediments within lakes and ocean basins are of great interest because sediments provide a record of past climatic fluctuations and weathering processes in the source region. Many small or dry lakes of the western Great Basin were once extensive Pleistocene lakes and contain sensitive indicators of paleoclimate in their sedimentary record (Benson et al., 1990; Smith and Street-Perrott, 1983). Regional climatic variations can be constrained by determining lake sediment provenance using new techniques for tracing the dissolved and suspended loads of streams feeding the intermontane basins of the west. The trace element chemistry and isotopic composition of sediments in fluvial, lacustrine, and marine environments have become useful tools in determining sediment provenance and source rock age and chemistry. The rare earth elements (REE) comprise a group of trace elements (lanthanum through lutetium) whose chemical properties systematically change across the periodic table from the lightest to the heaviest elements (Byrne and Sholkovitz, 1996; Sholkovitz and Szymczak, 2000). This systematic variation, combined with sensitivity to redox changes and adsorption/complex formation, makes the REE valuable tools for studying weathering reactions in terrestrial environments as well as chemical processes operating in rivers, estuaries, and oceans (Elderfield et al., 1989; Öhlander et al., 1996; Sholkovitz and Szymczak, 2000). Dissolved and suspended loads transported in the Owens River and its tributaries are deposited in Owens Lake, eastern California, and accumulate

over time as siliciclastic and carbonate lake sediments. Isotopically distinct igneous and metasedimentary source rocks drained by a network of perennial streams, which feed an intermittently closed basin, have resulted in a nearly complete sedimentary record spanning the past ~800 ka in the Owens Lake drainage basin. Hence, this large and regionally important drainage basin is an ideal environment to investigate the sources, transport, and deposition of REE. Moreover, paleoclimate proxies in sediments from Owens Lake, and other Great Basin lakes, reflect variations in precipitation and temperature associated with changing jet stream patterns over the during Great Basin glacial periods.

While isotopes of strontium (Sr) and neodymium (Nd) (one of the REE) are useful tracers of sediment provenance, little is known about Nd isotope and REE systematics in freshwater systems. In a novel approach to sediment provenance and paleoclimate studies, we use the Nd isotopic composition of the chemical and clastic sediments in Owens Lake, eastern California, to investigate these topics. The goals of this work are to use the Nd isotopic record contained in lacustrine carbonates to study the paleoclimatic history of the Owens Lake drainage basin, and to elucidate the partitioning behavior of Nd, and the other REE, in fresh water systems.

## 2. BACKGROUND

### 2.1 Geologic and hydrologic setting

Owens Valley is ideally suited for regional paleoclimatic investigations using lacustrine sedimentary records. The valley is a north-south trending intermontane basin sealed by Tertiary volcanic rocks on its southern end, and consequently traps runoff, originating primarily in the eastern Sierra Nevada range, in Owens Lake. Owens Valley was formed during Late Tertiary extension in the Great Basin, which contributed to the tectonic uplift and tilting of the Sierra Nevada range. These characteristics have resulted in a continuous sedimentary record of Late Tertiary erosion of the eastern Sierran Nevada in Owens Lake.

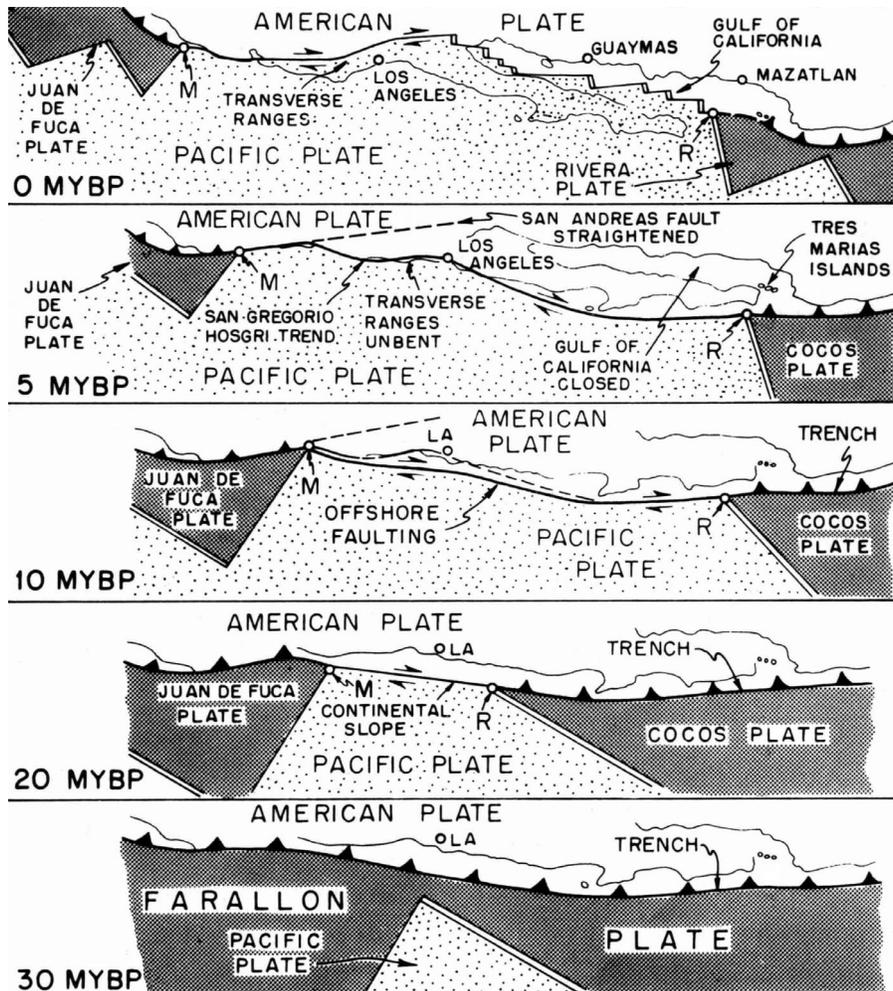
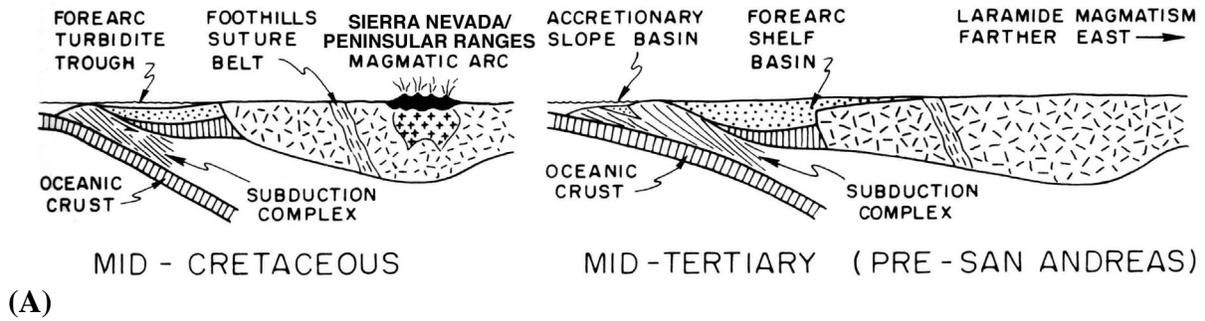
#### *2.1.1 Regional tectonic framework*

The Pacific-North American plate has evolved through four major tectonic plate boundary regimes. During the Latest Pre-Cambrian to Early Cambrian time, rifting of the western margin of the North American plate induced classic miogeoclinal sedimentation along an Atlantic-type passive margin (Dickinson, 1981; Moores et al., 1999). Subsequently, a Japanese-style margin, with an offshore island arc and marginal sea, developed along the western North American plate. The Late Paleozoic/early Mesozoic Antler and Sonoma orogenies occurred during this Japanese-style tectonic setting, and most likely reflect collisions between offshore island arcs and the Early Paleozoic Atlantic-type continental margin (Dickinson, 1981). Erosional remnants of sediments deposited along the Pacific-North American plate margin during these two tectonic regimes occur as roof pendants capping plutons in the east central Sierra Nevada range (Stevens and Greene, 1999). The nature and composition of these roof pendants will be discussed in detail in section 2.1.2. The onset of an Andean-type margin during

the Mid-Late Mesozoic developed an arc-trench system with an eastward-dipping subduction zone and a corresponding terrestrial volcanic chain above what would eventually become the Sierra Nevada batholith (Figure 1a) (Dickinson, 1981). Concurrent emplacement and metamorphism of the Franciscan mélangé assemblage, deposition of the sedimentary Great Valley sequence in the arc-trench gap, and emplacement of the Sierra Nevada batholith (SNB) and Peninsular Ranges Batholith (PRB) occurred from the Late Jurassic to Late Cretaceous during this penultimate tectonic setting (Dickinson, 1981). Arc magmatism subsided as steep (Sevier-style) subduction shifted to shallow (Laramide-style) subduction of the Farallon Plate during Paleocene and Eocene time (Dickinson, 1981). Progressive subduction of the Farallon-Pacific spreading ridge under the North American Cordillera brought the Pacific plate into contact with the North American plate along the present California-type plate margin, forming the San Andreas fault system (Figure 1b) (Dickinson, 1981). Although the two major California batholiths (SNB and PRB) were created in the same magmatic arc, they have since been dissected and displaced by strike-slip motion along the San Andreas fault system. Oligocene and Miocene extension has separated fault blocks in the Great Basin by distances ranging from 10 to 150 km through imbricate normal faulting (Wernicke, 1992). This style of extension formed the N-S trending basins of eastern California, which include Owens, Panamint, and Death Valleys.

### *2.1.2 The Sierra Nevada batholith*

The Sierra Nevada batholith is part of a northwest trending chain of Mesozoic plutonic intrusions extending from Baja California, through the Mojave Desert, to the Sierra Nevada Mountains, and terminating in western Nevada (Bateman and Wahrhaftig, 1966). The west side of the Sierra Nevada is a long, gently westward-dipping slope, which is contrasted on the east side by a steep, normal fault scarp resulting from the uplift and tilting of the Sierra Nevada



(B)

**Figure 1.** (A) Schematic cross-section of successive stages of the Mesozoic-Cenozoic Andean-type plate margin along the Pacific North American plate. Note the emplacement of the Sierra Nevada batholith. (B) Map view of the Paleo/Neogene tectonic development of the Pacific-North American plate. Figures from Dickinson (1981).

batholith. The batholith is comprised of discrete plutons, approximately 90% of which are Cretaceous in age and range in areal extent from approximately 1 km<sup>2</sup> to greater than 1000 km<sup>2</sup> (Saleeby, 1999). Compositions vary from quartz diorite in the western Sierras to granite in the east (Ague and Brimhall, 1988; Bateman and Wahrhaftig, 1966; Saleeby, 1999). The dominant rock compositions are quartz monzonite and granodiorite in roughly equal parts. Small bodies of mafic and ultramafic rocks including diorite, quartz diorite, and hornblende gabbro occur as inclusions within, septa between, or as small roof pendants capping individual plutons (Bateman and Wahrhaftig, 1966). In the eastern portion of the batholith these mafic masses are associated with Paleozoic metasedimentary rocks and the Triassic and Jurassic granitoids which intrude them (Bateman, 1983; Bateman and Wahrhaftig, 1966). Quartz diorite and granodiorite units contain plagioclase, quartz, orthoclase, amphibole, and biotite with accessory magnetite, ilmenite, and sphene (Ague and Brimhall, 1988). Quartz monzonite and granite generally contain significant amounts of microcline, rather than orthoclase, with accessory muscovite and subhedral garnet (Ague and Brimhall, 1988). Sulfide minerals in the Sierra Nevada Batholith are rare, but pyrrhotite, pyrite, and chalcopyrite may exist in anhedral or interstitial crystal forms, as well as inclusions within magnetite or amphibole (Ague and Brimhall, 1988).

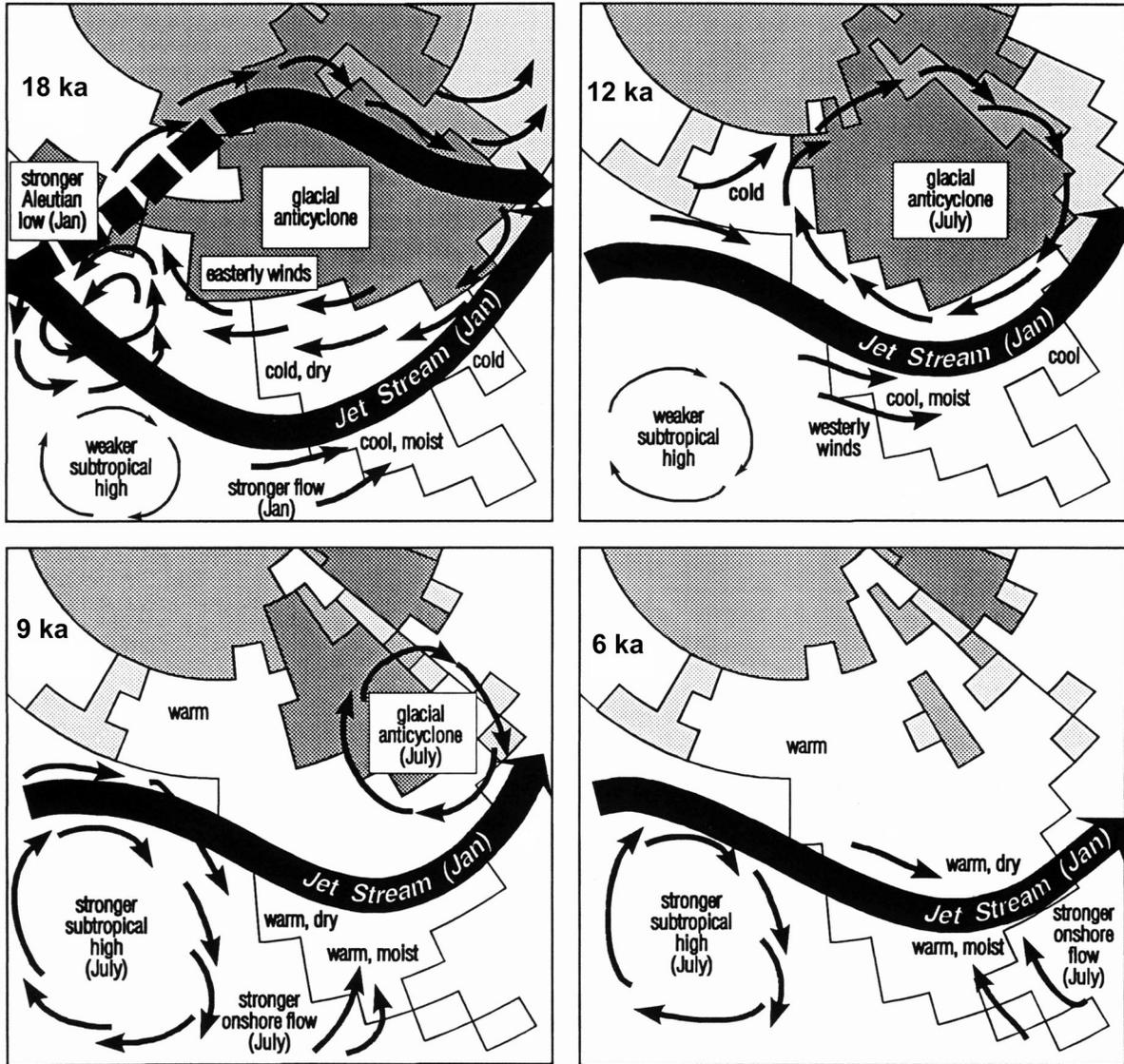
Remnants of the Paleozoic metasedimentary belt, which is characterized by greenschist facies regional metamorphism and Mesozoic volcanic and metavolcanic rocks, occur along the southwestern foothills of the batholith and as small roof pendants along the crest of the east-central Sierra Nevada (Bateman and Wahrhaftig, 1966). Nokleberg (1983) identified six separate, stratigraphically distinct, fault-bounded terranes composing the Sierra Nevada batholith, which he hypothesized were accreted to the North American continent intermittently between pulses of magmatism throughout the late Cretaceous period. In the eastern Sierra

Nevada, roof pendants within what Nokleberg (1983) referred to as the Owens and the High Sierra terranes are drained by streams flowing into the Owens River, and eventually into Owens Lake. The Owens terrane is dominated by Cambrian to Silurian metasandstone, pelitic hornfels, and minor marble and calc-silicate hornfels (Nokleberg, 1983). The High Sierra terrane is dominated by Permo-Triassic metavolcanic rocks and Mississippian to Permian pelitic hornfels, marble, calc-silicate hornfels, and minor quartzite (Nokleberg, 1983). The Mount Morrison roof pendant is a Paleozoic section more than 9700 m thick located along the southern edge of Long Valley Caldera, southeast of Mammoth Lakes, and constitutes the most complete and areally extensive roof pendant present in both the eastern Sierra Nevada and the Owens Valley drainage basin (Bateman and Wahrhaftig, 1966). Eastern Sierra Nevada roof pendants within the Owens Valley drainage basin are irregularly shaped, typically disconnected rock bodies; however, their unique mineralogy and chemistry could have significant impacts on the chemical and clastic sediment contained in the Owens Lake record.

### *2.1.3 Late Tertiary/Holocene paleoclimate of western North America*

Stratigraphic pollen records, macrofossil assemblages, and lake-level records have been used to reconstruct regional climate in western North America since 18 ka ago (Thompson et al., 1993). From ~18 to 16 ka temperatures in the southwestern United States were ~10°C lower than today and pluvial lakes in the Great Basin were filling (Thompson et al., 1993).

Precipitation at this time was augmented as the Westerly jet stream was split, with the southern branch deflected to the south, in response to Easterlies induced by the Laurentide ice sheet anticyclone (Figure 2) (Thompson et al., 1993). The southern branch of the jet stream carried moist air masses over the American southwest (Thompson et al., 1993). Ice sheets and alpine glaciers retreated in this region by ~12 ka in response to moderating precipitation and

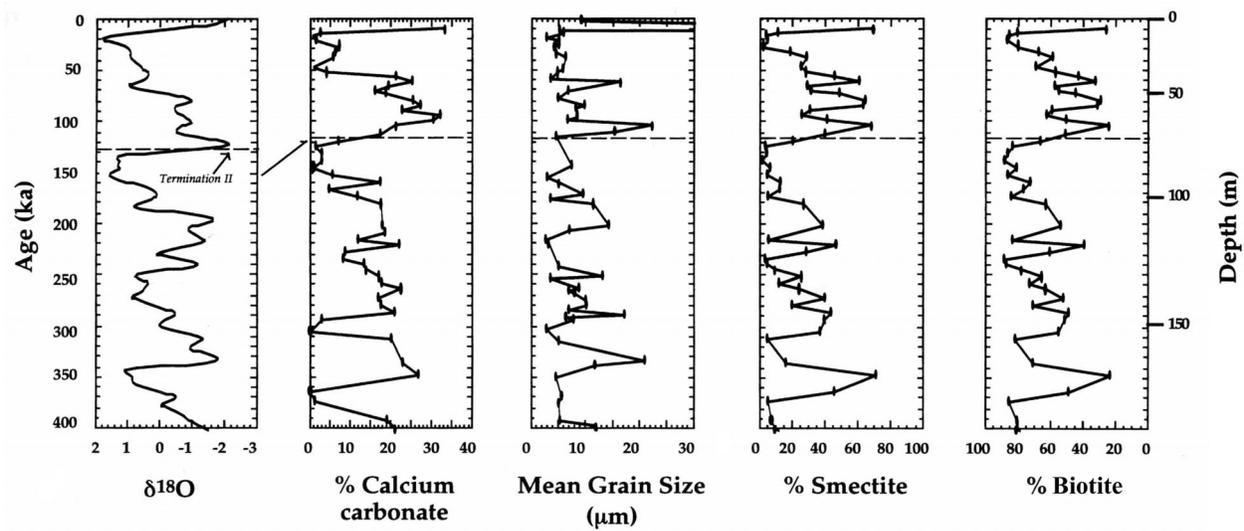


**Figure 2.** Estimates of major changes in atmospheric circulation over the last 18 ka for western North America as simulated by the Community Climate Model of the National Center for Atmospheric Research. Figure from Thompson et al. (1993).

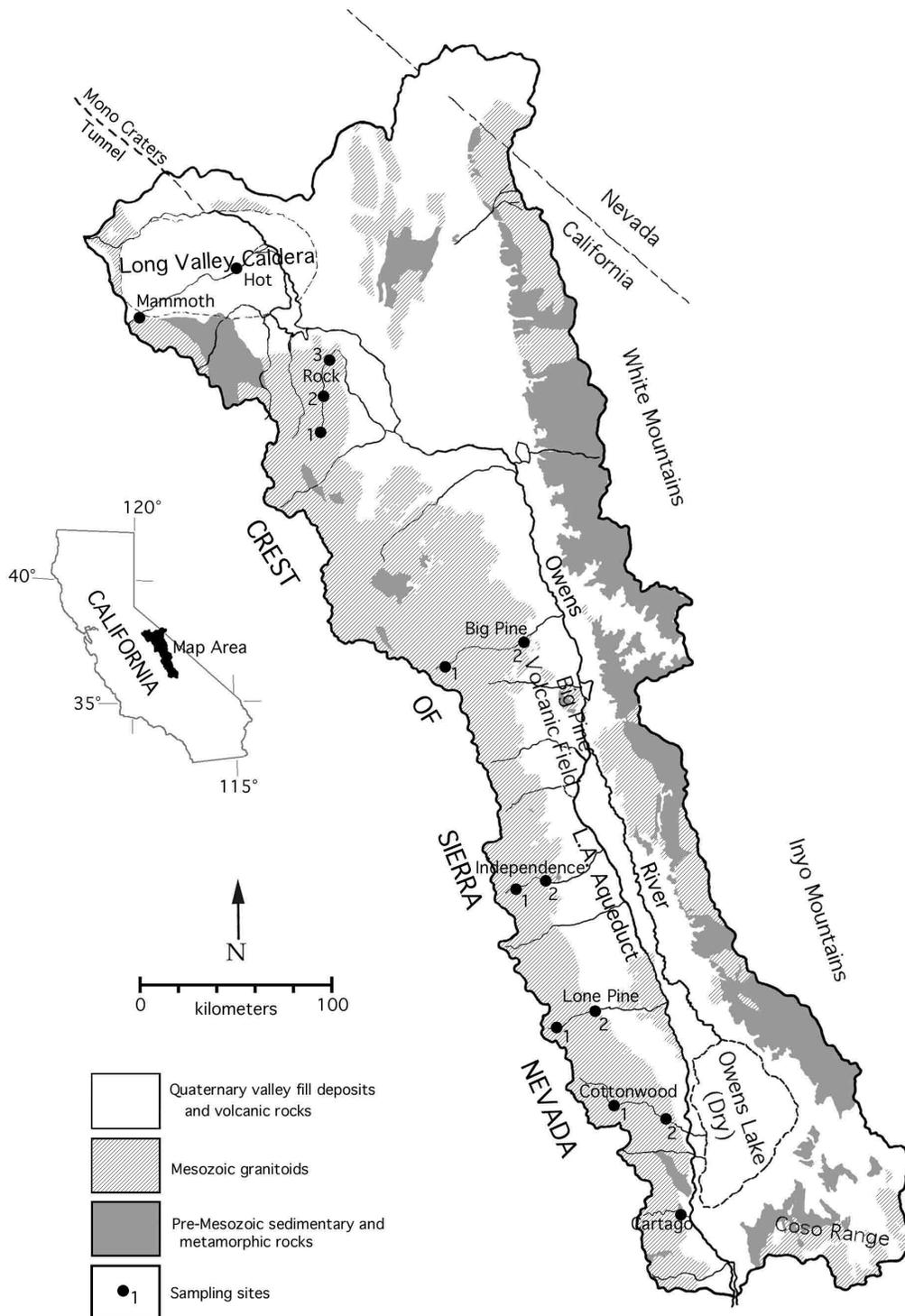
temperatures (Thompson et al., 1993). During the glacial-interglacial transition ~12 ka, portions of the western interior, and perhaps Owens Valley, experienced drier conditions as the jet stream shifted northward in response to the retreating Laurentide ice sheet (Thompson et al., 1993). This allowed summer monsoonal precipitation to reach the southern portions of the American southwest (Thompson et al., 1993). Precipitation was still higher than present-day values at this time. California and the American northwest experienced their driest Holocene conditions ~9-6 ka, whereas the Great Basin and the southwest deserts experienced their driest Holocene conditions ~6-3 ka (Thompson et al., 1993). Climate in the eastern Sierra Nevada range and Owens valley, as reflected in paleoclimate proxies taken from the Owens Lake record, coincide with the marine oxygen isotope record, suggesting conditions responsible for global climate cycles are the same as those responsible for eastern Sierran glaciation (Figure 3). The Owens Lake paleoclimate record will be discussed in detail in section 2.2.

#### *2.1.4 Owens Valley physiography*

Owens Valley is the western-most structural graben of the Great Basin. The Valley is a long, narrow, closed basin bound on the west by the Sierra Nevada Mountains, on the northeast by the White and Inyo Mountains, on the north by a volcanic plateau composed primarily of 0.76 Ma Bishop Tuff, and on the southeast by the volcanic Coso Range (Figure 4). The valley floor is composed of thick sequences of unconsolidated to moderately consolidated alluvial fan, transition-zone, glacial, talus, volcanic, fluvial, and lacustrine deposits which are overlain in places by Quaternary volcanic rocks and cinder cones (Hollett et al., 1991). Plutons of the Sierra Nevada are thought to be continuous across the valley floor, under both the Quaternary valley fill and large portions of the White and Inyo mountains (Hollett et al., 1991).



**Figure 3.** Comparison of deep-sea sediment  $\delta^{18}\text{O}$  record to four paleoclimate proxies from Owens Lake core OL-92, plotted against age. Note: (1) similarity between Owens Lake proxies and the marine record; (2) the delayed response to the oxygen isotope stage 6/5 boundary (Termination II); and (3) the reversed X-axes for  $\delta^{18}\text{O}$  and biotite. Taken from Menking (1997b).



**Figure 4.** Generalized geology, hydrology, and physiography of the Owens Lake drainage basin (after Hollett et al., 1991). Labeled streams were sampled at sites indicated by filled circles.

Tertiary uplift and tilting of the Sierra Nevada batholith during Basin and Range faulting, in conjunction with an increasingly moist and cool climate associated with changing atmospheric circulation (see section 2.1.3), triggered alpine glaciation in the region as recent as 0.4 ka ago (Hollett et al., 1991). Late Pleistocene moraine complexes exist in all of the major valleys originating in the Sierra Nevada (Phillips et al., 1996). Glaciation produced abundant sediments which have been transported to the valley floor by perennial streams in the Sierra Nevada, providing the dominant source of the valley fill (Hollett et al., 1991). Ephemeral streams and debris flows in the White and Inyo mountains transport a much lesser amount of detritus to the valley floor (Hollett et al., 1991).

Climate and hydrology in Owens Valley is influenced greatly by the Sierra Nevada mountain range. Moisture-laden air masses originating in the northern Pacific are forced up over the Sierra Nevada, cooled by the orographic effect, and precipitate their moisture as snow or rain in the Sierra Nevada primarily from October to April (Hollett et al., 1991). Consequently a “rain shadow” occurs in Owens Valley, and all areas east of the crest of the Sierra Nevada, causing the region’s semiarid to arid climate (Hollett et al., 1991). Average annual precipitation at the crest of the Sierra Nevada exceeds 100 cm, whereas average annual precipitation on the valley floor is approximately 13 to 15 cm (Hollett et al., 1991). The White and Inyo mountains receive approximately 18 to 36 cm of precipitation per year (Hollett et al., 1991). Evidence from the Owens Lake core (OL-92) indicating precipitation in the Sierra Nevada and White-Inyo ranges has varied as a function of climate will be discussed in section 2.2.

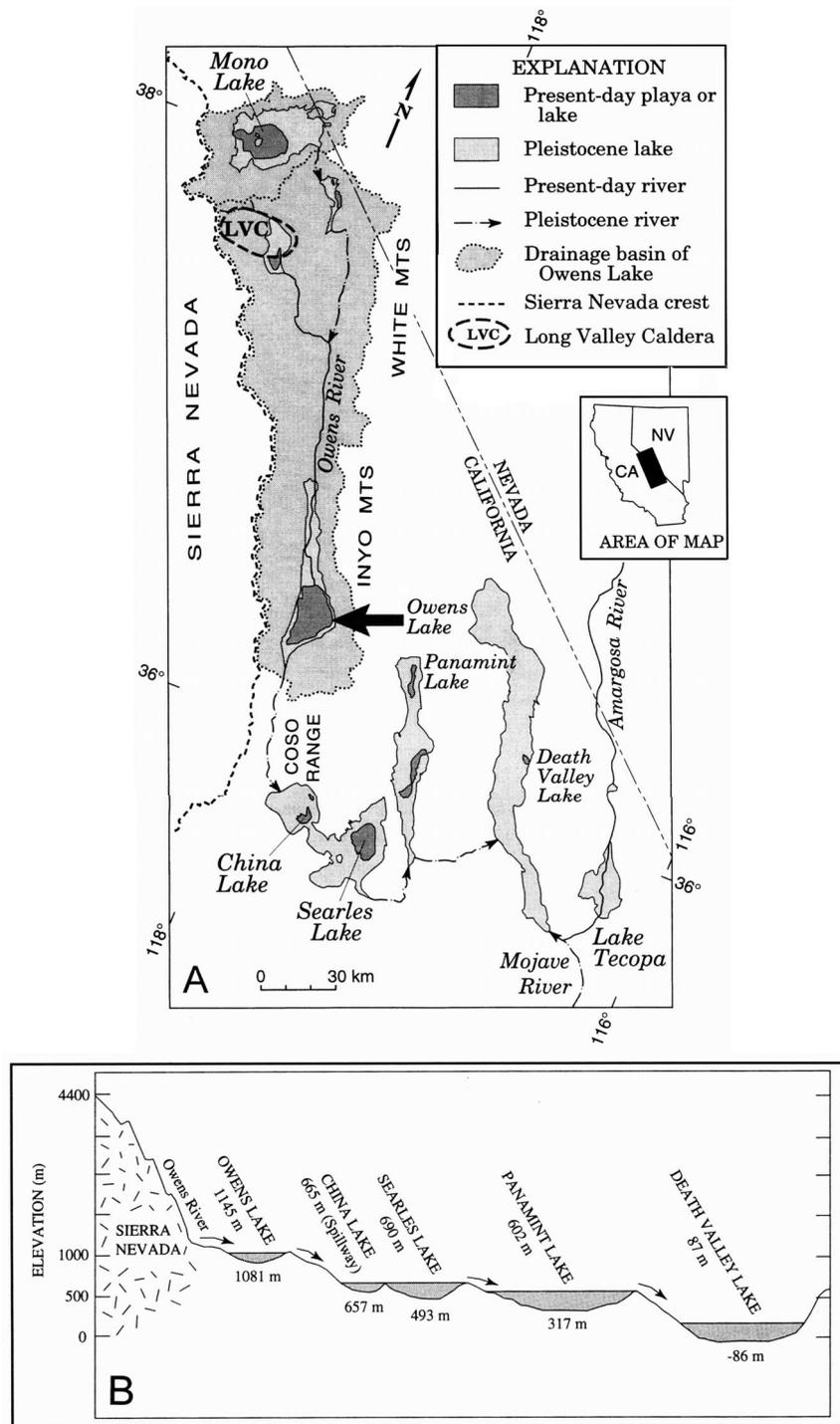
#### *2.1.5 Owens River system*

Owens Lake is the present terminus for surface water, groundwater, and eroded sediment within the Owens Valley drainage basin. During Pleistocene pluvial stages, this drainage basin

was linked at various times with Mono, Adobe, Long, Indian Wells, Searles, Panamint, and Death Valleys which lie adjacent to the north, south, and east of Owens Valley (Figure 5)(Jannik et al., 1987; Smith, 1984). Owens Lake is a remnant of a larger Pleistocene Lake Owens (Smith, 1984). Glacial episodes in the Sierra Nevada have been correlated with pluvial periods in Owens Valley when lakes in Indian Wells, Searles, and Death Valleys received overflow from Lake Owens (Smith, 1984).

The Owens River, fed by perennial tributaries from the Sierra Nevada and ephemeral tributaries from the White and Inyo Mountains, is the main drainage, or “trunk stream”, for all surface water in the Owens Valley drainage basin (Hollett et al., 1991). Approximately 16 km south of Big Pine, water from the Owens River is diverted into the Los Angeles Aqueduct system and is transported south toward Los Angeles, diverting any additional tributaries along its path (Hollett et al., 1991). Prior to the development of the Los Angeles Aqueduct system in 1913, Owens Lake was a saline lake about 24 km long, 16 km wide, and 9 m deep (Sharp and Glazner, 1997). At its greatest extent, Owens Lake was 76 m deep, covering nearly twice its area prior to diversion (Sharp and Glazner, 1997).

Owens River chemistry is controlled by the chemistry of its tributaries and the chemistry of hydrothermal fluids circulating through Long Valley Caldera. Hot springs contributing  $\leq 1\%$  of the total discharge of Himalayan rivers have been shown to have a significant impact on solute chemistry and radiogenic Sr budget (Evans et al., 2001). Similarly, Pretti and Stewart ( *in press*, 2001) determined hydrothermal activity and weathering of Paleozoic metasedimentary roof pendants in the Owens Lake drainage basin govern the Sr budget in the Owens Lake drainage basin.

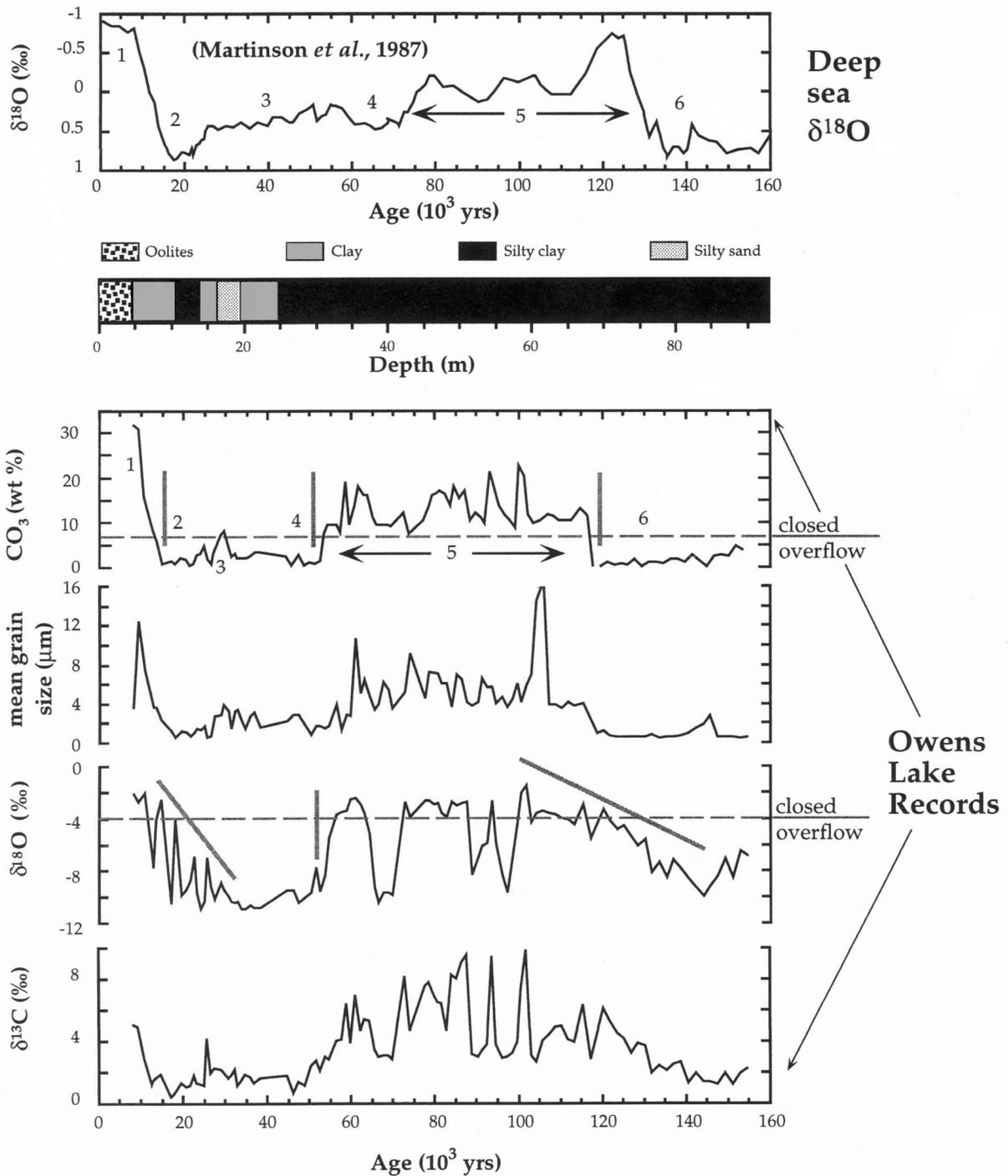


**Figure 5.** (A) Map view of Pleistocene lakes and drainage patterns in Owens Valley and adjacent basins. (B) Schematic cross-section of Pleistocene lake chain. (Figures from Smith and Bischoff, 1997)

## 2.2 Core OL-92

Owens Lake is the final repository for sediments being shed off the eastern Sierra Nevada, and its continuous chemical and clastic sedimentary record makes Owens Lake an ideal location to study Quaternary climate change in the Sierra Nevada. In April-June 1992, the United States Geological Survey (USGS) drilled core OL-92 to a depth of 322.86 m in Owens Lake as part of a Pleistocene age-lake core-drilling program developed by the USGS in 1991 (Smith and Bischoff, 1997). A roughly linear time-depth curve has been generated for the entire core based on a constant average mass accumulation rate, which is constrained by radiocarbon dates, bulk density reconstruction, and paleomagnetic events from within the core (Bischoff et al., 1997b). The core represents approximately 800 ka of deposition in Owens Lake, and is dominated by lacustrine sediments (Smith, 1997). The lower 117 m of the core are predominantly silt and clay with several sand beds, and have a mean grain size fluctuating between 10 and 130  $\mu\text{m}$ , indicating moderately deep and shallow conditions (Menking, 1997b; Smith, 1997). The overlying 201 m of silt and clay have a mean grain size between 2 and 22  $\mu\text{m}$ , and indicate deep-water conditions (Menking, 1997b; Smith, 1997). The uppermost 5-6 m of the core are composed of an oolitic layer nearly 4 m thick overlain by a salt bed resulting from the anthropogenic desiccation of the lake (Smith, 1997). Smectite, chlorite, and kaolinite are the primary clay minerals present in the core, although clay-sized quartz, plagioclase, and K-feldspar are also present (Menking, 1997b). Pedogenic and authigenic smectite dominates the clay-sized fraction of closed-lake sediments (sediments deposited during relatively dry interglacial periods while Owens Lake was not overflowing), while detrital biotite, quartz, and feldspar dominate the clay-sized fraction of spilling-lake sediments (sediments deposited during pluvial periods when the lake was spilling over to downstream lakes) (Bischoff et al., 1997c; Menking, 1997b).

The oxygen isotopic composition, average sediment grain size, and sediment mineralogy of Owens Lake each respond at different rates to changes in the regional climate (Figure 6). Therefore, the estimated timing of climatic oscillations in the Sierra Nevada is proxy-dependant for Owens Lake sediments, and care must be taken when correlating such terrestrial climate records with the marine oxygen isotopic record (Menking, 1997a). However, these records indicate periods of overflow in Owens Lake that correspond to glacial episodes in the adjacent Sierra Nevada range. Solutes delivered by the ancestral Owens River were concentrated in Owens Lake by evaporation during drier, closed-lake conditions. Deposition rates of calcium carbonate increased during these periods, preserving higher concentrations of calcium carbonate in the lake's sedimentary record. Owens Lake sediments are fine grained with low concentrations of calcium carbonate from 154 to 120 ka and from 50 to 15 ka, indicating overflowing conditions persisted during these intervals (Menking, 1997a). Carbonate content and grain size is variable from 120 to 50 ka, but this interval is dominated by high carbonate and coarse-grained sediments, indicating mostly-closed conditions with a few brief periods of overflow (Menking, 1997a). All climate change proxies reflect the desiccation of Owens Lake from ~15 ka to the present (Menking, 1997a). These data indicate the last glacial maximum in the Sierra Nevada range occurred ~21 ka ago.



**Figure 6.** Paleoclimate proxies from Owens Lake sediments compared to the marine oxygen isotope record of Martinson et al. (1987) over the last 160 ka. Heavy gray lines represent the different responses of the carbonate content and the  $\delta^{18}\text{O}$  proxies to climate changes associated with the 6/5, 5/4, and 2/1 oxygen isotope stage transitions (From Menking, 1997a).

### 2.3 Radiogenic isotopes and the REE

Radiogenic isotopes form from the decay of radioactive isotopes, and are useful geochronologic tools and geochemical tracers. Isotopes of strontium and neodymium have significantly higher atomic masses than the stable isotopes of hydrogen, carbon, and oxygen, and therefore isotopic fractionation due to evaporation or other chemical reactions is small and easily corrected (Stille and Shields, 1997). Different isotopic reservoirs within the Earth are characterized by unique strontium and neodymium isotope ratios due to the parent-daughter fractionation of Rb-Sr and Sm-Nd which took place during the differentiation of the earth (Stille and Shields, 1997). Differentiation of the earth produced continental crustal rocks, which are enriched relative to the mantle, in Rb and Nd. Therefore, the  $^{87}\text{Sr}/^{86}\text{Sr}$  of continental crustal rocks ( $>$  approx. 0.715) will be higher than mantle-derived rocks (approx. 0.702-0.704), whereas the  $^{143}\text{Nd}/^{144}\text{Nd}$  of continental crustal rocks (approx. 0.5110-0.5125) will be lower than that of mantle-derived rocks (approx.  $>$  0.5125) (Faure, 1986; Stille and Shields, 1997). The strontium and neodymium isotopic composition of a mineral should be identical to the fluid phase from which the mineral crystallized, and, hence, can be used to determine its source (Stille and Shields, 1997). The isotopic composition of chemical sediments precipitating from Owens Lake, therefore, reflect the isotopic composition of the lake at the time the sediments formed.

Studies investigating the REE composition and chemistry of major rivers have provided important information about the extent of elemental fractionation between colloidal, dissolved, and particulate phases, as well as solution pH and ionic strength controls on REE solubility (Goldstein and Jacobsen, 1988a; Goldstein and Jacobsen, 1988b; Goldstein and Jacobsen, 1988c; Tricca et al., 1999). Prior to 1990, the concentration of REE in river waters was assumed to match mean concentrations in continental shale (Elderfield et al., 1989). Subsequent work has

demonstrated shale-normalized differences between light REE (LREE) and heavy REE (HREE) in rivers, oceans, and estuaries (Sholkovitz and Szymczak, 2000; Sholkovitz et al., 1999). The net effect of chemical reactions taking place in shallow estuaries, where suspended particles and bottom sediment strongly interact, is a net HREE enrichment of river water as it enters the ocean (Sholkovitz et al., 1999).

Sediment fluxes from major rivers will locally influence the REE isotopic composition of sea water (Sholkovitz and Szymczak, 2000; Sholkovitz et al., 1999). Differences in the Sr and Nd isotopic composition of ocean water among major ocean basins can only exist if the residence time of dissolved forms of these elements is shorter than the mixing time of the ocean water (Byrne and Sholkovitz, 1996). The residence time of Sr in seawater ( $\sim 10^6$  years) is several orders of magnitude greater than the mixing time of ocean water ( $\sim 1000$  years), whereas Nd (and presumably the other REE) has a significantly shorter residence time ( $\sim 200$  to  $1000$  years) (Piepgras and Wasserberg, 1982; Tachikawa et al., 1999). Therefore, neodymium ( $t_{1/2} = 1.06 \times 10^{11}$  years) and other nuclides, which originate in isotopically distinct source regions and have sufficiently short residence times in sea water, are useful tracers of oceanic circulation patterns and mixing rates (Andersson et al., 2001; Piepgras and Wasserberg, 1982). The residence time of Sr and Nd in lacustrine systems is less well understood. Sedimentary rocks preserve the Nd isotopic composition of the rocks from which the sediments were derived, although isotopic systematics can sometimes be disturbed by diagenesis or metamorphism (Bock et al., 1994; Linn and DePaolo, 1993; Patchett et al., 1999).

### 3. FIELD AND LABORATORY METHODS

#### 3.1 Stream water samples

In order to constrain inputs into the Owens Lake system, waters were sampled from a variety of streams within the Owens Lake drainage basin. Water samples were collected from eight creeks draining the eastern Sierra Nevada Mountains in May 2000. Major drainages were sampled at points near the top and bottom of the catchment. Water samples were filtered through acid-washed 0.45  $\mu\text{m}$  (142 mm diameter) nitrocellulose membrane filters mounted in a polycarbonate filter holder. Approximately 0.5 L of water was filtered to flush the filter apparatus before samples were collected. Approximately one liter of filtered water was collected in acid-cleaned high density polyethylene bottles for isotopic and major and trace element analysis. Water samples were acidified by adding concentrated Seastar® ultra-pure nitric acid to make a 1% solution.

Geographic position at each sampling site was determined using a hand-held Garmin 12XL GPS unit (Table 1). Stream discharge was determined by measuring the stream width at each site and using a Flow Probe hand-held flow meter to measure water velocity and stream depth in segments across the stream (Table 1). Stream flow was averaged for segments of roughly equal depth. Alkalinity was determined in the field using a Hach digital titration kit (Table 1). Phenolphthalein indicator was added to 100 mL of stream water, which were collected in a pre-contaminated 125 mL Erlenmeyer flask. The sample was titrated with 1.6 N sulfuric acid to a colorless endpoint and alkalinity was read from the hand-held digital titrator. Specific conductance and stream temperature were determined with a hand-held Oakton TDS/Conductivity meter (Table 1). The meter was calibrated with standard conductivity solutions and conductivity and temperature were measured by immersing the calibrated electrode

**Table 1.** Field measurements of stream waters draining the eastern Sierra Nevada Mountains. Equipment failure (resulting in loss of data) at selected sites is indicated by (--).

Sample	Elevation* (m)	Site Location†	pH (unadjusted)	Discharge (L s <sup>-1</sup> )	Conductivity (μS)	Water T (°C)	Alkalinity (mg L <sup>-1</sup> as CaCO <sub>3</sub> )
Rock Cr. #1	2951	N37° 27' 22.0" W118° 44' 05.9"	--	2620	18.98	6.8	72.1
Rock Cr. #2	2719	N37° 29' 34.3" W118° 43' 03.8"	--	2674	28.8	7.3	20
Rock Cr. #3	2455	N37° 32' 16.0" W118° 42' 05.0"	7.75	4376	33.1	9.9	17.5
Big Pine #1	2408	N37° 07' 30.0" W118° 26' 14.5"	--	3958	37.6	9.7	15.4
Big Pine #2	1555	N37° 07' 57.8" W118° 20' 06.3"	7.76	192	54.9	21.8	25.7
Lone Pine #1	2548	N36° 35' 07.1" W118° 14' 28.2"	7.22	472	25.3	8.3	11.8
Lone Pine #2	1817	N36° 35' 50.0" W118° 11' 16.7"	7.38	1585	31.5	6.6	14.9
U. Cottonwood #1	2959	N36° 27' 34" W118° 09' 50"	7.30	765	18.23	5.7	7.6
U. Cottonwood #2	2953	N36° 27' 34" W118° 09' 50"	7.25	2066	11.06	--	8.6
L. Cottonwood	1596	N36° 26' 23.4" W118° 04' 54.1"	7.52	4510	23.1	--	16.9
Cartago Cr.	1227	N36° 18' 37.3" W118° 02' 37.5"	8.00	31	72.3	17.2	36.1
Independence #1	2785	N36° 46' 25.7" W118° 20' 12.1"	7.35	1304	32.9	6.2	13.7
Independence #2	1981	N36° 47' 13.4" W118° 17' 51.7"	7.16	2304	49.5	10.5	18.7
Mammoth Cr.	2737	N37° 35' 59" W118° 59' 45"	7.28	1126	35.6	5.7	15.0
Twin Lakes Falls	2627	N37° 36' 47.1" W119° 00' 33.8"	7.38	1536	27.3	4.6	12.1
Hot Cr.	2114	N37° 40' 25.7" W118° 48' 36.8"	8.19	7330	480	25.0	143.5

\* relative to sea level

† Based on WGS-84 map datum

directly into the stream. Stream pH was determined using a hand-held VWR pH/Temp meter (Model 2000) calibrated with pH 4.0 and pH 7.0 buffer solutions (Table 1). The pH electrode was immersed directly into the stream and pH was read from the meter. 200 mL aliquots of the stream water samples were analyzed using a Spectro inductively coupled plasma – atomic emission spectrometer (ICP-AES) for calcium, magnesium, sodium, potassium, strontium, barium, silicon, aluminum, iron, sulfur, and phosphorus. Analyses were conducted according to the U.S. EPA analytical method 6010B guidelines (E.P.A., 1996). Elemental concentrations were determined by averaging three measurements per element for each sample.

A 100  $\mu$ L aliquot of a mixed spike solution containing  $^{87}\text{Rb}$ ,  $^{87}\text{Sr}$ ,  $^{150}\text{Nd}$ , and  $^{147}\text{Sm}$  was added to a 5 mL aliquot of stream water for analysis by isotope dilution thermal ionization mass spectrometry (ID-TIMS). The remaining volume of water was evaporated to dryness. To isolate strontium (Sr) from other elements, the evaporated sample was redissolved in a small volume of 3.0 N nitric acid and eluted through quartz columns filled with SrSpec resin. The isotopic composition of the separated Sr was determined by thermal ionization mass spectrometry (TIMS) after loading approximately 400 ng of Sr onto rhenium single filaments for analysis on a Finnigan MAT 262 thermal ionization mass spectrometer.

### **3.2 Core samples**

Core OL-92 comprises three sub-cores of which nine channel samples representing a 10 cm length of core sediment were removed and shipped to the University of Pittsburgh by K. Menking (Vassar College) in May of 2001 (Table 2). Prior to shipment, the samples were washed twice in deionized water to remove sodium bicarbonate. At the University of Pittsburgh, the samples were leached with ammonium acetate buffered at pH 8.2 to remove exchangeable cations, rinsed with Milli-Q water, and subsequently leached with 8% acetic acid (HOAc) to

**Table 2.** Age and proportion of carbonate in samples taken from USGS core OL-92. (--) indicates datum not available.

OL-92 sub-core*	Sample Depth (m)	Carbonate (%) <sup>†</sup>	Age (ka)
OL-92-3	3.52-3.62	67	6.9
OL-92-3	4.82-4.92	60	9.2
OL-92-1	7.5-7.6	7.4	13.9
OL-92-1	8.5-8.53	6.6	15.6
OL-92-1	9.5-9.6	8.8	16.8
OL-92-1	11.1-11.3	9.8	18.8
OL-92-1	13.5-13.6	21	21.8
OL-92-1	15.9-16.0	--	24.4
OL-92-1	18.1-18.2	--	28.1

\*Core OL-92 is made up of three sub-cores: OL-92-1 (5.49-61.37m), OL-92-2 (61.26-322.86m), OL-92-3 (0.00-7.16m)

<sup>†</sup>Based on mass leached during acetic acid treatment

isolate the HOAc-leachable fraction (presumably carbonate) and residue (presumably silicate) of the samples. The silicate residue was dissolved using a closed-container, concentrated hydrofluoric and perchloric acid digestion procedure. A 200  $\mu\text{L}$  aliquot of a mixed spike solution containing  $^{87}\text{Rb}$ ,  $^{87}\text{Sr}$ ,  $^{150}\text{Nd}$ , and  $^{147}\text{Sm}$  was added to an aliquot approximately equal to 1 mg of carbonate of the HOAc-leachable material to determine the concentration of Rb, Sr, Sm, and Nd by ID-TIMS. A 500  $\mu\text{L}$  aliquot of the same mixed spike solution was added to an aliquot approximately equal to 2 mg of silicate residue to determine Rb, Sr, Sm, and Nd by ID-TIMS. Strontium and the rare earth elements (REE) were subsequently separated from the remaining silicate residue and HOAc-leachable fractions using cation exchange resin in quartz columns. To obtain the cleanest Sr sample possible, the Sr cuts from the cation columns were eluted through SrSpec® resin in Teflon columns. The neodymium in the REE cut was separated from the other REE by eluting both sample fractions through quartz columns filled with LnSpec® resin. Approximately 400 ng of Sr was loaded onto rhenium single filaments with tantalum oxide ( $\text{Ta}_2\text{O}_5$ ), and 50-100 ng of Nd was loaded onto rhenium double filaments with 1.0 N hydrochloric acid. The Sr and Nd isotopic composition of the samples was determined by TIMS.

## 4. RESULTS

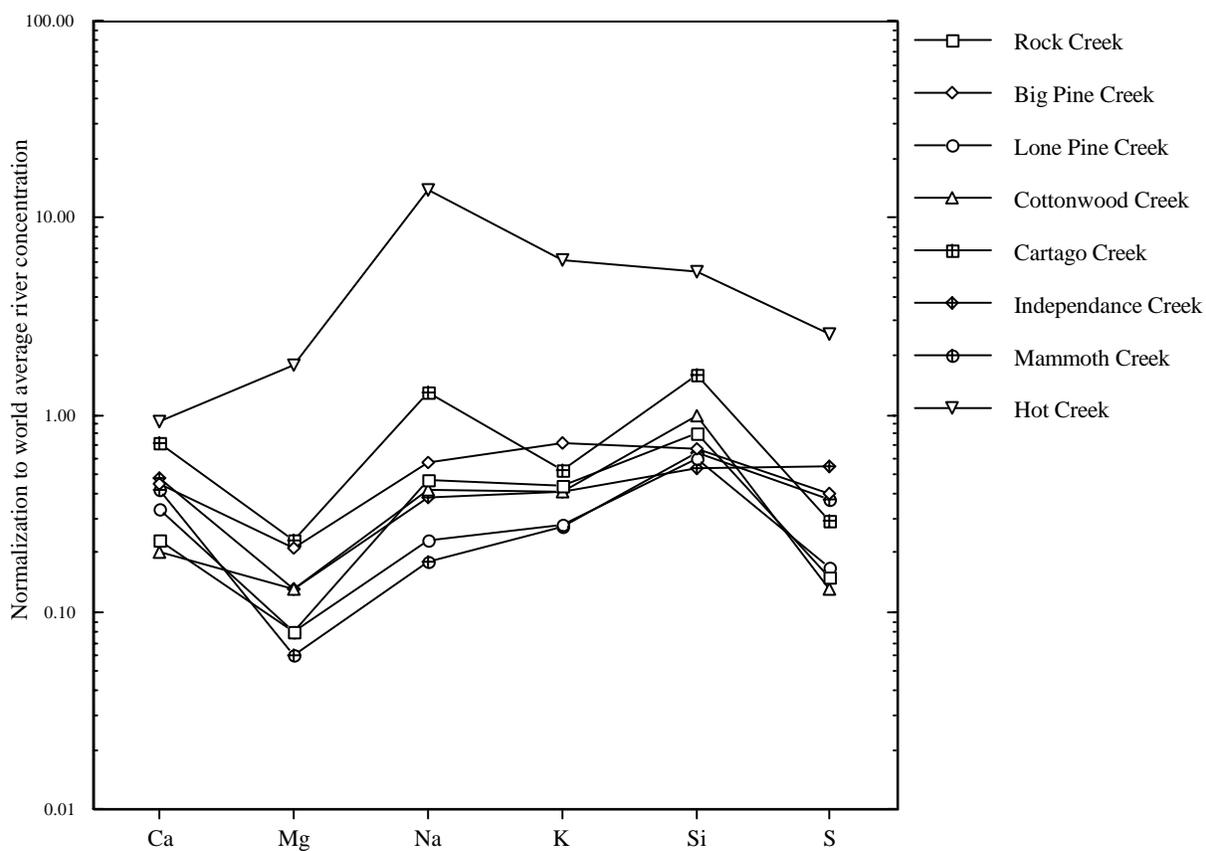
### 4.1 Stream water samples

Eastern Sierra Nevada streams are characterized by near neutral pH values ranging from 7.2 to 8.2 (Table 1). Streams in the southern, more arid, portion of Owens Valley generally have a higher dissolved load than those in the northern portion of the drainage basin (Table 3). The introduction of hydrothermal fluids into Hot Creek as it flows across Long Valley Caldera increases its dissolved load to approximately  $300 \text{ mg L}^{-1}$ , the highest of the eight drainages we sampled, and an order of magnitude above its source waters at Twin Lakes Falls and Mammoth Creek (Table 3). The total dissolved load for most samples ranges from 13 to  $41 \text{ mg L}^{-1}$  (Table 3). Water samples representing the same stream were averaged and normalized to the world river average reported by Berner and Berner (1996) for each major solute in order to reveal variations in individual solutes not caused by inherent differences between streams in contrasting climates. With the exception of Hot Creek and Cartago Creek, eastern Sierra Nevada stream water is relatively dilute, with concentrations of Mg and S in some streams more than an order of magnitude below the world average (Figure 7). Runoff originating in basins characterized by steep slopes, little vegetation, and young debris, similar to those in the high eastern Sierra, has been shown to have low concentrations of base cations, dissolved silica, and alkalinity, and are attributed to the short hydrologic residence times and poor soil development in these areas (Clow and Sueker, 2000). Hot Creek has higher concentrations of all major cations except Ca, with more than 10 times the world average Na concentration. Cartago Creek is the southernmost stream sampled in this study, and it flows through actively grazed pastures and riparian areas. Inputs of animal waste directly into Cartago creek may contribute the creek's anomalous Na value. World average-normalized plots of solutes in Cottonwood Creek, Independence Creek,

**Table 3.** Concentrations of major and trace elements in stream waters draining the eastern Sierra Nevada Mountains. Elemental concentrations were determined by ICP-AES unless otherwise noted. Note: Upper Cottonwood Creek samples taken from same stream location. (<DL) indicates value is less than instrument detection limit. (--) indicates datum not available due to instrument failure or is still being processed.

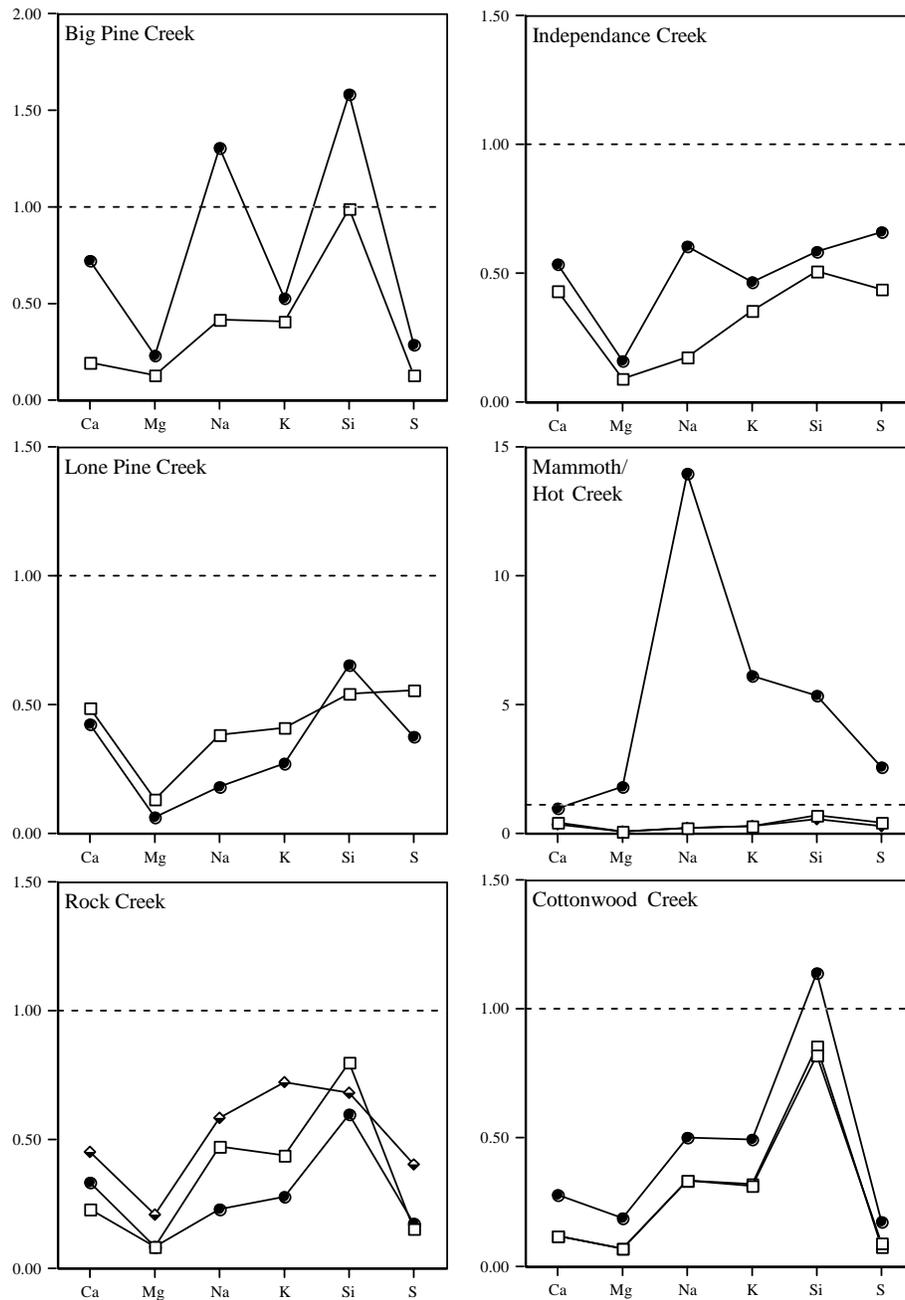
Stream Site	Ca	Mg	Na	K	Sr	Ba	Si	Al	Fe	S	P	Rb*	Sr*	Sm*	Nd*	TDS
	----- $\mu\text{mol L}^{-1}$ -----											----- $\text{nmol L}^{-1}$ -----				$\text{mg L}^{-1}$
Rock Cr. #1	61	6.3	57	10	0.10	0.028	93	0.65	0.67	5.5	0.27	9.4	98	0.0086	0.44	--
Rock Cr. #2	78	12	124	15	0.14	0.025	153	0.46	0.86	17	0.29	--	--	--	--	--
Rock Cr. #3	87	15	141	18	0.17	0.033	167	0.62	0.95	16	0.34	13	160	0.029	0.19	--
Big Pine #1	119	18	98	18	0.18	0.034	103	1.0	<DL	32	0.33	7.5	170	0.016	0.13	19
Big Pine #2	18	42	164	30	0.31	0.065	134	2.0	<DL	37	0.39	18	300	0.0040	0.10	28
Lone Pine#1	107	6.8	38	6.4	0.25	0.028	89	1.9	0.61	12	0.24	14	350	0.0073	0.046	13
Lone Pine #2	116	17	66	12	0.31	0.032	118	1.5	<DL	17	0.11	13	230	0.0047	0.030	17
U. Cottonwood #1	40	10	75	10	0.23	0.026	142	2.2	1.22	8.0	0.22	20	220	0.019	0.22	15
U. Cottonwood #2	41	9.7	75	11	0.24	0.030	148	1.9	1.11	6.6	0.24	19	220	--	0.25	14
L. Cottonwood	94	26	114	16	0.44	0.051	197	0.94	1.09	15	0.47	16	420	--	0.25	22
Cartago Cr.	242	32	297	18	1.4	0.18	275	1.4	0.44	25	0.18	11	100	0.0067	0.21	41
Independence #1	144	13	39	12	0.25	0.038	88	2.4	<DL	38	0.29	7.3	230	0.025	0.18	18
Independence #2	177	22	135	15	0.36	0.043	101	2.4	<DL	57	0.33	7.0	330	0.0093	0.15	26
Mammoth Cr.	170	6.1	45	8	0.14	0.082	126	0.79	<DL	43	0.20	6.3	130	--	0.12	21
Twin Lakes Falls	111	10	38	10	0.14	0.054	98	1.7	0.46	21	0.22	8.7	130	0.011	0.15	15
Hot Cr. #2	312	253	3150	203	1.1	0.18	926	1.6	<DL	221	6.5	470	100	0.008	0.21	220

\*Determined by isotope dilution thermal ionization mass spectrometry (ID-TIMS)

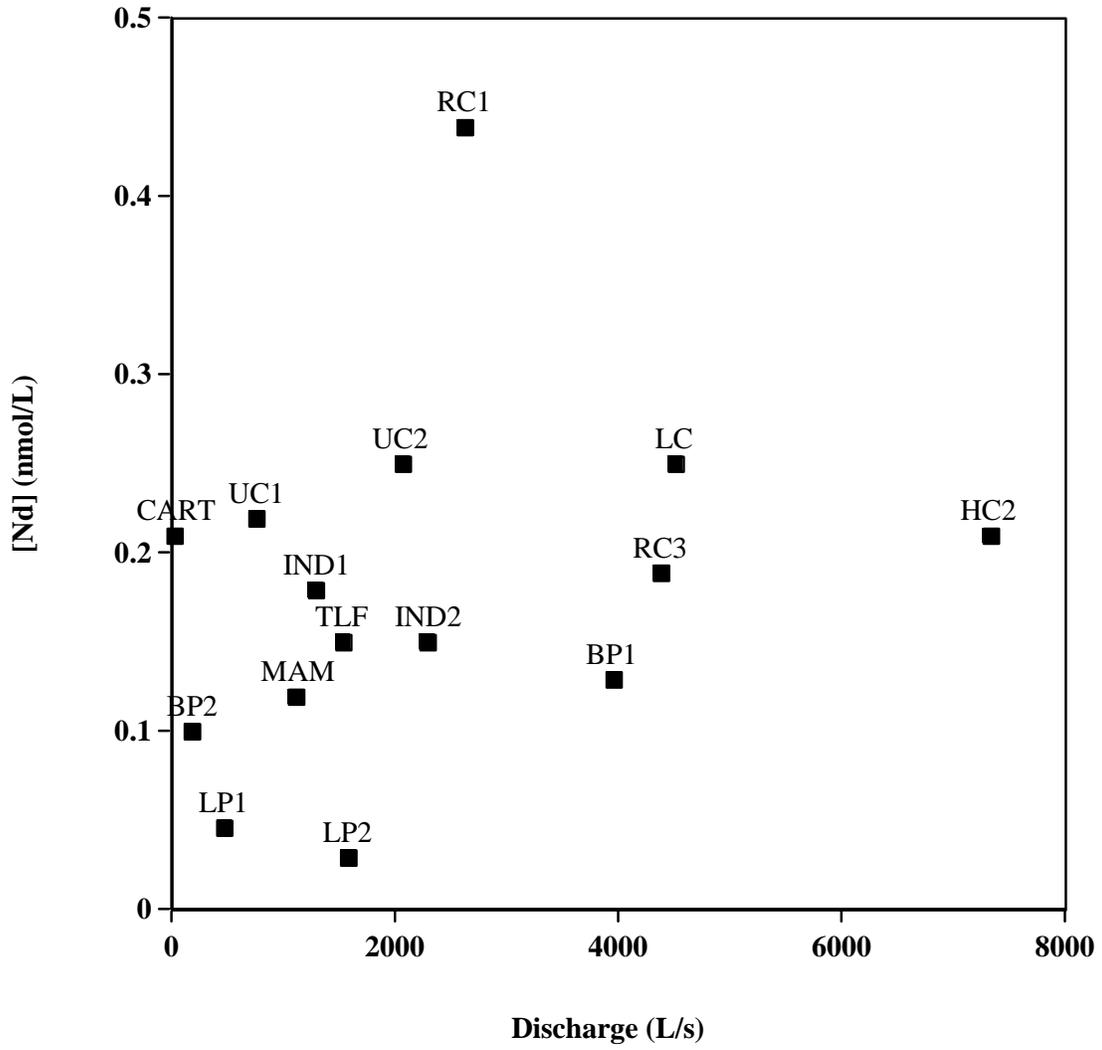


**Figure 7.** Patterns of world river average-normalized dissolved solute concentrations for eight major drainages of the eastern Sierra Nevada. Points represent averaged values for samples from same stream. Figure 8 presents same plot for individual streams. Note: Upper Cottonwood #1 was not included in the Cottonwood Creek calculation.

and Big Pine Creek reveal increased solute concentrations in samples taken from the lower reaches of their watersheds (Figure 8). Water entering these streams at lower portions of their drainage basin, after interacting with solute-laden soil solutions and soluble minerals in the granitic bedrock, contain relatively high concentrations of dissolved solids which increase the dissolved load of the trunk stream. Mammoth creek flows into Lake Mary along its southeast shore, flows out along the northwest shore at Twin Lakes Falls, and eventually forms Hot Creek as it meanders across Long Valley Caldera. A five- to nearly fifteen-fold increase in major solutes at the Hot Creek site is caused by mixing of solute-rich hydrothermal solutions with the relatively dilute waters from Mammoth Creek and Twin Lakes Falls (Goff et al., 1991). Samples taken from Lone Pine Creek and Rock Creek at downstream sites, where discharge is higher, are more dilute than samples taken at upstream sites. A similar inverse relationship between discharge and dissolved load is seen in the Frasier River, Canada, and is attributed to dilution of mineral-rich groundwater by snowmelt (Cameron, 1996). Pretti and Stewart (*in press*, 2001) sampled the same creeks, except Cartago and Twin Lakes Falls in March and July 1999, as part of a Sr-isotopic study of stream water in Owens Valley. In all cases, their reported values for total dissolved solids were higher than those determined in this study. Samples taken in March may not have been exposed to the seasonal snowmelt present in May when the samples were collected for the present study. Concentrations of Nd were less than  $1 \text{ nmol L}^{-1}$  in all streams, and were not correlated with stream discharge (Figure 9). The samples were too dilute to concentrate and separate an adequate amount of Nd for isotopic analysis.



**Figure 8.** Patterns of world average-normalized solute concentrations for six drainages of the eastern Sierra Nevada. Open boxes represent upstream sites, closed circles represent downstream sites, and half-filled diamonds are samples taken in between the up- and downstream sites. Mammoth Creek flows into Hot Creek, and are plotted together. Figure 7 presents averaged values for each stream plotted against the same world average-normalized scale.



**Figure 9.** Variation in Nd concentration with stream discharge. Data labels correspond to stream sites in Table 3.

## 4.2 Core samples

### 4.2.1. Elemental concentrations

The proportion of HOAc-leachable material in the core samples increases from approximately 10% at the last Sierran glacial maximum (see section 2.2) to ~70% at 6.9 ka, reflecting the onset of the present interglacial period and subsequent desiccation of Owens Lake (Table 2) (Bischoff et al., 1997a). Strontium, samarium, and neodymium are strongly partitioned into the HOAc-leachable fraction of the core samples, whereas rubidium is concentrated in the silicate residue (Tables 4 and 5; Figure 10). The concentration of Nd in the HOAc-leachable fraction of Owens Lake sediments is 10 to 100 times higher than those found in marine planktonic foraminifera, which record the Nd isotopic composition of contemporary seawater, and roughly 10 times higher than bulk sediment values associated with these foraminifera (Burton and Vance, 2000; Vance and Burton, 1999). Rubidium is consistently an order of magnitude more concentrated in the silicate residue than in the HOAc-leachable fraction of each of the core samples (Table 4). Strontium concentrations decrease from 1700 ppm at 24 ka to 240 ppm at 16 ka before increasing to 3600 ppm at 7 ka in the HOAc-leachable fraction of the core samples (Figure 10). Patterns of Sm and Nd concentrations mimic one another in both core sample fractions (Table 5). Concentrations of Sm and Nd in the HOAc-leachable fraction are roughly equal to their corresponding concentrations in the silicate residue for the shallowest samples; however, at depths greater than 4.92 m, concentrations of Sm and Nd are 2 to 5 times higher in the HOAc-leachable fraction than in the silicate residue (Figure 10).

### 4.2.2 Isotope ratios

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the HOAc-leachable material resemble that of modern seawater

**Table 4.** Rb and Sr concentrations and isotopic composition of Owens Lake core samples. (--) indicates datum not available.

Depth (m)	HOAc leachate			Residue		
	Rb* (ppm)	Sr* (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}^\dagger$	Rb* (ppm)	Sr* (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}^\dagger$
3.52-3.62	0.56	3600	0.709136±09	15	47	0.708790±11
4.82-4.92	0.95	1800	0.709116±08	65	160	0.708373±09
7.5-7.6	32	450	--	140	260	--
8.5-8.53	21	240	--	--	--	--
9.5-9.6	10	550	0.709247±09	180	250	0.708897±09
11.1-11.3	9.2	700	--	180	230	--
13.5-13.6	16	850	0.709272±11	240	280	0.709474±10
15.9-16.0	12	1700	0.709194±09	240	270	0.709118±10
18.1-18.2	--	--	--	190	270	--

\*Determined by isotope dilution mass spectrometry.

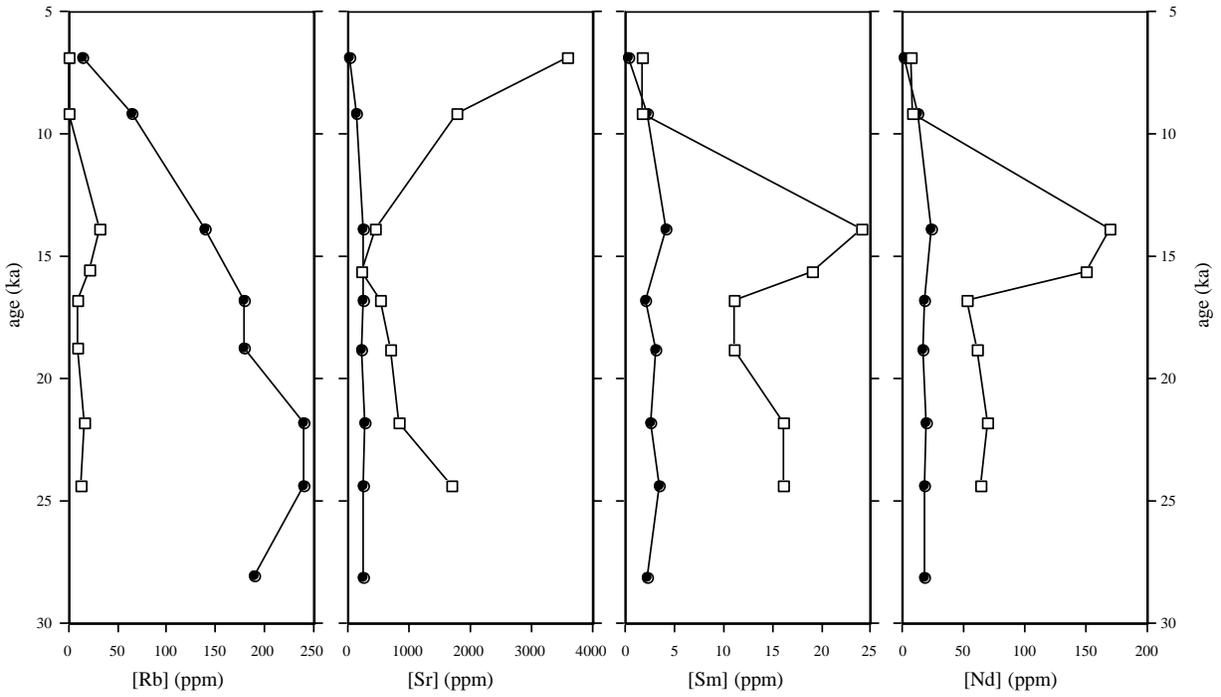
†Uncertainty shown is in-run 2-sigma uncertainty; estimated external reproducibility is 20 ppm.  
University of Pittsburgh value for SRM 987 is 0.71024.

**Table 5.** Sm and Nd concentrations and isotopic composition of Owens Lake core samples. (--) indicates datum not available.

Depth (m)	HOAc leachate			Residue		
	Sm* (ppm)	Nd* (ppm)	$\epsilon_{Nd}^{\dagger}$	Sm* (ppm)	Nd* (ppm)	$\epsilon_{Nd}^{\dagger}$
3.52-3.62	1.7	7.1	-6.31	0.29	1.6	-6.35
4.82-4.92	1.7	7.8	-6.53	2.2	12	--
7.5-7.6	24	170	-5.46	4.1	24	-6.47
8.5-8.53	19	150	-5.71	--	--	--
9.5-9.6	11	53	-5.84	2.0	18	-7.00
11.1-11.3	11	61	-5.74	3.0	16	-6.88
13.5-13.6	16	69	-5.97	2.6	20	-6.71
15.9-16.0	16	64	-5.75	3.4	18	-6.98
18.1-18.2	--	--	--	2.2	18	-6.60

\*Determined by isotope dilution mass spectrometry

$\dagger$ Relative to  $^{145}\text{Nd}/^{144}\text{Nd}$  CHUR = 0.511847



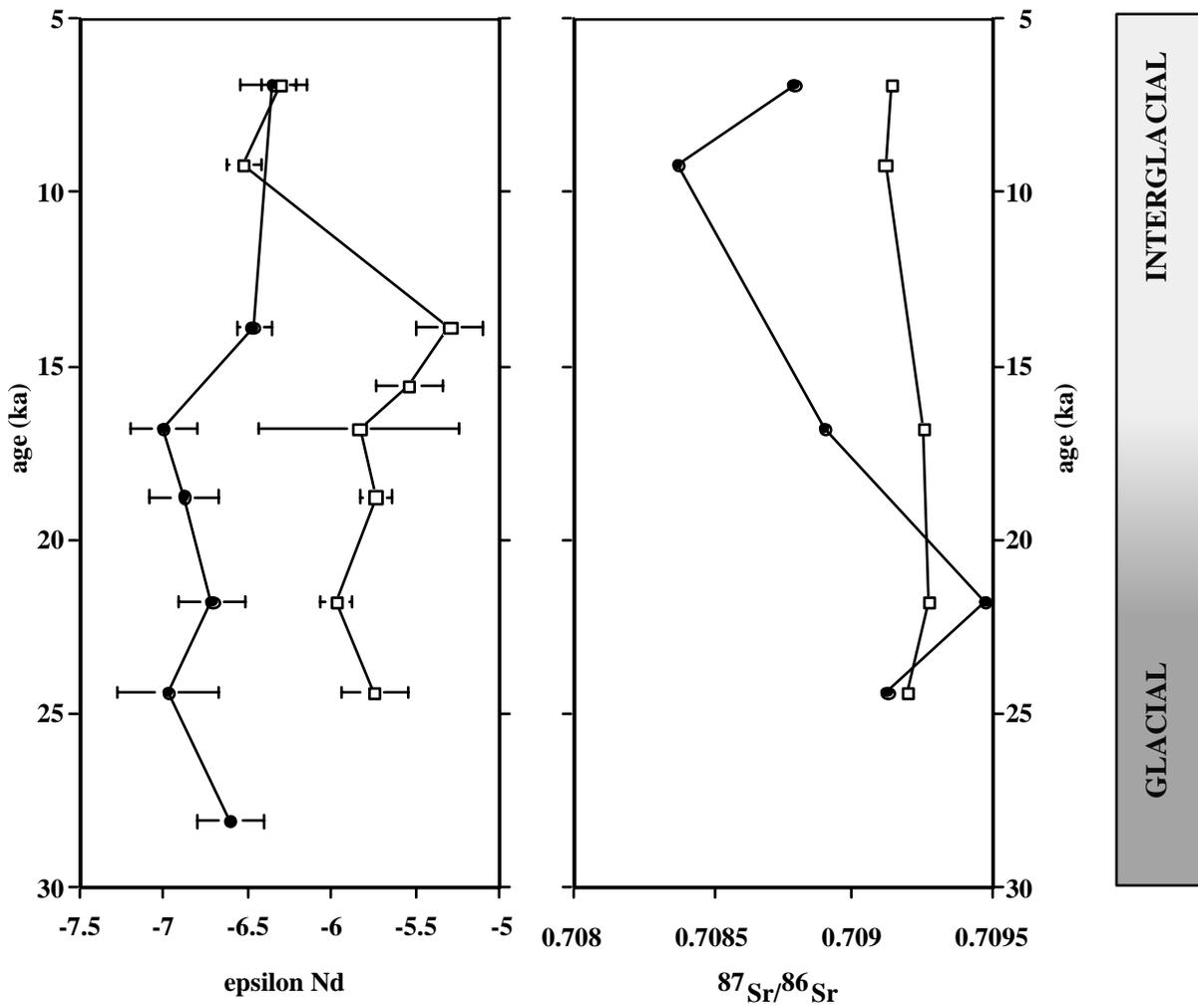
**Figure 10.** Concentrations of Rb, Sr, Sm, and Nd in Owens Lake core OL-92 sediment samples. Solid circles represent the silicate residue and the empty boxes represent the HOAc-leachable fraction.

(0.7092), whereas the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the silicate residue are slightly lower, or less radiogenic (Table 4). Pretti and Stewart (*in press*, 2001) determined the Sr flux-weighted  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of several streams in the Owens Lake watershed to be 0.70911. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios observed in the HOAc-leachable fraction of the core samples are clustered around this value, indicating a relatively unchanging Sr isotopic composition in Owens Lake water over the last 28 ka. However, significant differences are observed in the Sr isotopic composition of the silicate residue (Figure 11). The HOAc-leachable fraction and the silicate residue have similar  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from ~24 to 17 ka, near 0.709. After this time, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the silicate residue decreases below 0.7085 at ~9 ka before increasing again to values near 0.709 at 7 ka. The observed Sr-isotopic excursion below 0.7085 may be a result of changes in source rock lithology or watershed area. The Sr isotopic composition of Owens Lake sediments is weakly correlated with  $\epsilon_{\text{Nd}}$ , and age, indicating these isotopic systems are governed by similar processes in the Owens Lake system (Figure 12).

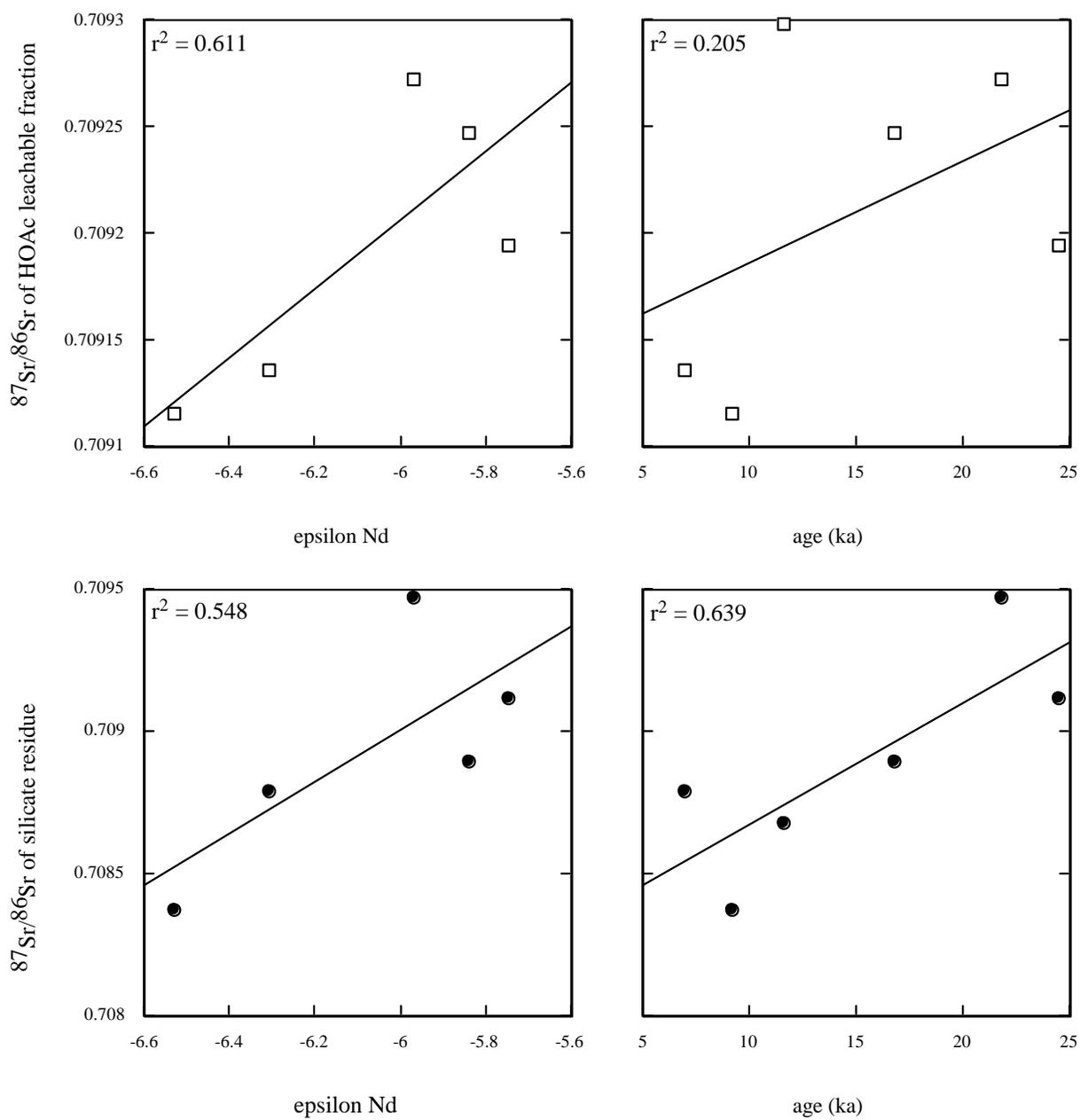
Neodymium isotope ratios are reported as  $\epsilon_{\text{Nd}}$  (Table 5) where:

$$\epsilon_{\text{Nd}} = \left[ \frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}}}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}} - 1 \right] 10^4 \quad (1)$$

CHUR is chondritic uniform reservoir, thought to represent a bulk solar system value. In sediments older than ~10 ka,  $\epsilon_{\text{Nd}}$  values for the HOAc-leachable fraction are approximately 1 epsilon unit higher than that of the silicate residue; however, in younger sediments, the  $\epsilon_{\text{Nd}}$  values for the HOAc-leachable fraction are less radiogenic, matching those of the silicate residue, near -6.5 (Figure 11). This shift may reflect a change in sediment source area or a change in source rock chemistry.



**Figure 11.** Variations in the Sr and Nd isotopic composition of sediment samples from Owens Lake core OL-92. Solid circles represent the silicate residue and open boxes represent the HOAc-leachable fraction.



**Figure 12.** Variations in the strontium isotopic composition of the HOAc-leachable fraction and silicate residue of Owens Lake sediments.

## 5. DISCUSSION

### 5.1 Causes of isotopic shifts in Owens Lake sediment

The difference in  $\epsilon_{Nd}$  of the chemical and clastic sediments in Owens Lake from ~30 to 12 ka, and subsequent downward shift of the chemical sediments after ~12 ka, indicates separate sources for the dissolved and suspended load of surface water reaching Owens Lake existed during this ~18 k.y. period. Potential causes of the offset between the dissolved and suspended loads include (1) different source regions for the dissolved and suspended load of the ancestral Owens River; (2) variations in the hydrothermal flux of streams flowing out of the Long Valley Caldera area; or (3) differential mineral weathering of Mesozoic granitoids in the sediment source region. These will be considered in turn.

#### 5.1.1 Siliciclastic sediment provenance

The two primary Sr and Nd reservoirs for sediments originating in the eastern Sierra Nevada range are Paleozoic metasedimentary rocks, which are restricted to several disconnected roof pendants, and abundant Mesozoic granitic rocks. Estimates of the Nd and Sr isotopic composition of these two reservoirs have been determined, and are distinct for each source rock and isotopic system (Table 6). Over the past ~30 ka, the Sr and Nd isotopic composition of clastic sediments in Owens Lake more closely resembles values characteristic of Mesozoic granitoids than they do Paleozoic metasedimentary rocks. This indicates streams supplying sediment to Owens Lake during last ~30 ka drained regions in the eastern Sierra Nevada underlain by Mesozoic granitoids, and the scattered Paleozoic roof pendants in the eastern Sierra Nevada do not significantly influence the overall isotopic composition of clastic material reaching Owens Lake. Moreover, clastic sediment in Owens Lake lacks detrital carbonate or

**Table 6.** Approximate Sr (Kistler and Peterman, 1973) and Nd (Linn et al., 1991) isotopic composition of Mesozoic granitic rocks and Paleozoic metasedimentary rocks of the Sierra Nevada range.

Source	Initial $\epsilon_{Nd}$ *	Initial $^{87}Sr/^{86}Sr$
Mesozoic granitoids	+7 to -6 <sup>†</sup>	0.704 to 0.708
Paleozoic metasedimentary rocks	-10 to -14	0.715 to 0.717

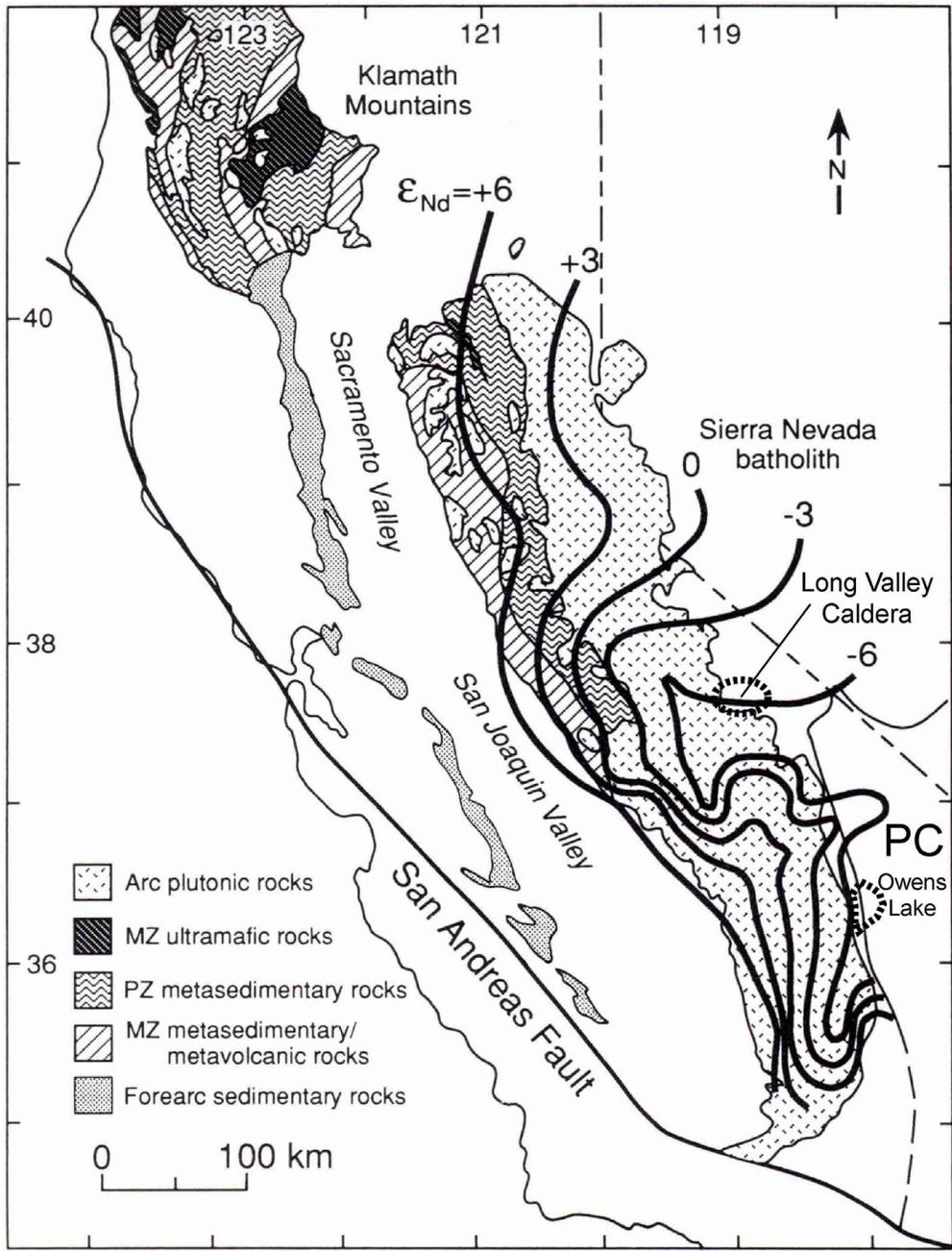
\* data reported as deviation of sample initial  $^{143}Nd/^{144}Nd$  from CHUR (Chondritic Uniform Reservoir)

<sup>†</sup> values decrease from west to east across the Sierra Nevada

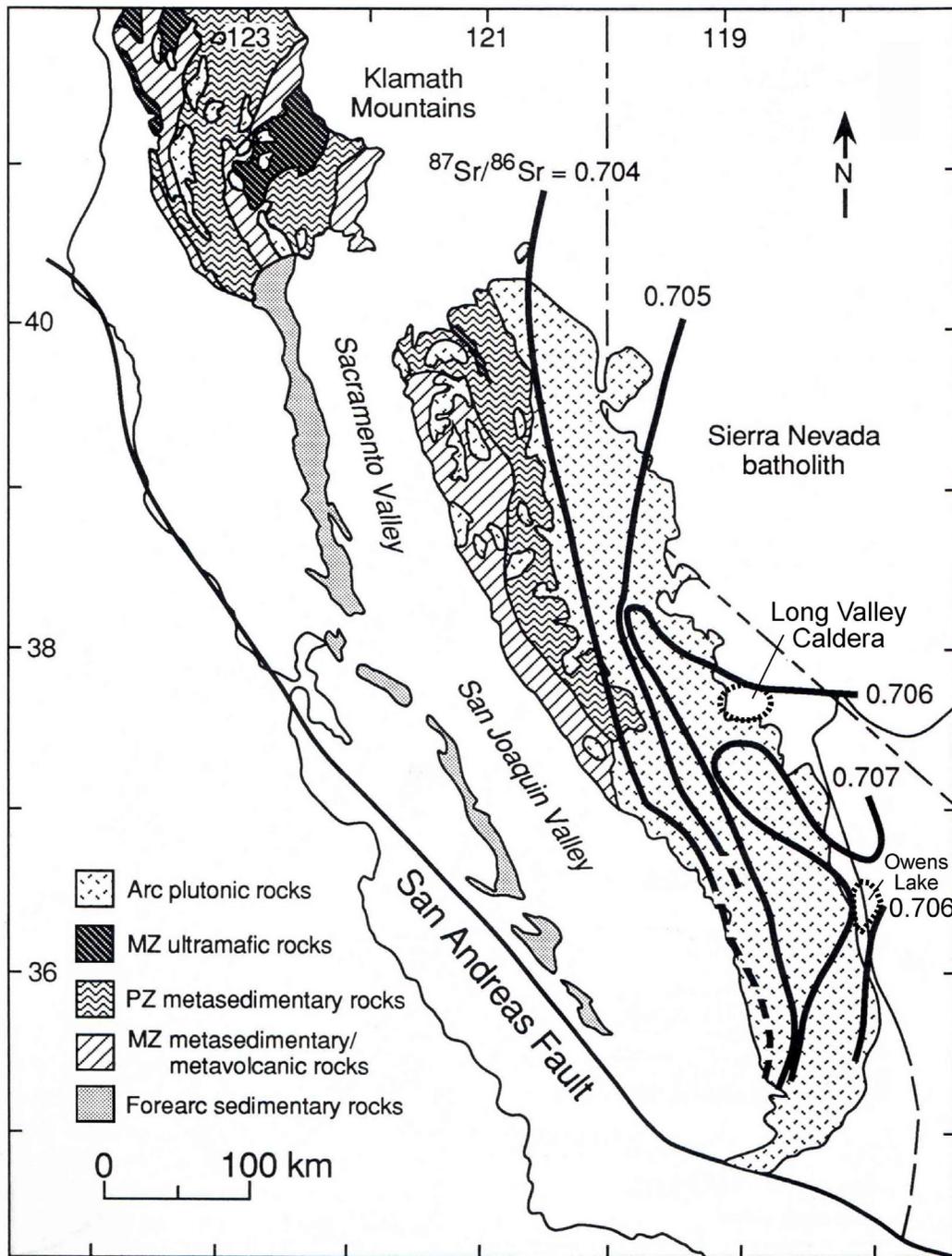
metamorphic minerals associated with sediments derived from metasedimentary rocks (Bischoff et al., 1997a).

Several studies have identified mineralogic, isotopic, and temporal west-east variations in the Sierra Nevada (Ague and Brimhall, 1988; Bateman, 1983; DePaolo, 1981). Plotted contours of isotopic variations in rocks of the Sierra Nevada batholith reveal a general southeast trend of decreasing  $\epsilon_{\text{Nd}}$  values and increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the northern Sierra Nevada range (Figures 13 and 14). The  $\epsilon_{\text{Nd}}$  value of plutons of the eastern Sierran crest in the vicinity of Owens Valley is variable, but  $\epsilon_{\text{Nd}}$  values less than -6.0, which correspond to values of clastic sediments found in Owens Lake over the past ~30 ka, for plutons in this region are likely. Chemical sediments in the lake at this time, however, are nearly one epsilon unit lower than the clastic sediments until ~12 ka, when the isotopic composition of the chemical sediments shifts to match that of the clastic sediments. The onset of interglacial conditions at this time, in response to the decreasing glacial anticyclone discussed in section 2.1.3, may have sufficiently altered precipitation patterns to cause a shift in the sediment source region for Owens Lake, and a subsequent isotopic shift in chemical sediments in the lake.

If, during pluvial periods, disproportionately high amounts of precipitation fell in the northern reaches of the Owens Lake drainage basin, excessive runoff from this region could have accounted for a majority of the water flowing into the ancestral Owens River, thereby governing the river's dissolved and suspended loads in the northern portion of the basin. Moreover, the Owens River maintains a gentle stream gradient as it meanders across Long Valley Caldera and the floor of Owens Valley, which may have allowed suspended material in the northern portion of the drainage basin to settle out of the river before it reached Owens Lake. If this was the case, a majority of the suspended material reaching Owens Lake at this time may have been



**Figure 13.** Contour map showing the regional variation of initial  $\epsilon_{Nd}$  for rocks of the Sierra Nevada range, eastern California (from Linn et al., 1992). MZ = Mesozoic, PZ = Paleozoic.



**Figure 14.** Contour map showing the regional variation of initial  $^{87}\text{Sr}/^{86}\text{Sr}$  for rocks of the Sierra Nevada range, eastern California (from Linn et al., 1992). MZ = Mesozoic, PZ = Paleozoic.

transported relatively short distances from local drainages in the southern portion of the basin. This scenario, in which the dissolved load is derived from the northern portion of the drainage basin and the suspended load is derived from the drainages immediately surrounding Owens Lake could account for the higher  $\epsilon_{Nd}$  values of the chemical sediment in Owens Lake from ~30 to ~12 ka. As the climate moderated and precipitation patterns across the eastern Sierra Nevada range changed, the contribution of dissolved and suspended material from the northern portion of the basin could have significantly decreased. After ~12 ka, precipitation in the southern portion of the drainage basin may have been high enough for streams in this region to become the dominant tributaries feeding the Owens River. This type of shift, from a dissolved load derived from the northern portion of the drainage basin, to a dissolved load derived from the southern portion of the drainage basin, may be responsible for the downward shift in the isotopic composition of Owens Lake chemical sediments at ~12 ka. This model is inconsistent with the onset of the cooler, moist climate across the Sierra Nevada range associated with the southward shift of the jet stream at ~12 ka (Figure 2). A warmer, drier climate doesn't occur in this region until after ~12 ka, as the glacial anticyclone weakens, and the jet stream migrates back toward the north. As changes in atmospheric circulation evolve over several ka, a precipitation-induced shift in the source region for Owens Lake sediments after ~12 ka will likely have insufficient time to produce the downward shift in the  $\epsilon_{Nd}$  values of Owens Lake chemical sediments which takes place by 9.2 ka.

### *5.1.2 Variations in hydrothermal activity*

Two prominent episodes of hydrothermal activity in Long Valley Caldera are recorded by hot-spring deposits and inactive thermal areas (Sorey et al., 1991). The oldest episode peaked at ~300 ka, whereas the younger episode began at ~40 ka and persists today (Sorey et al., 1991).

This current hydrothermal system may be related to the volcanic activity of the Mono-Inyo craters volcanic chain, which began ~40 ka ago. Temperature/depth patterns of two of the major aquifers in the caldera indicate a pulse of hydrothermal activity occurred approximately 3 ka ago (Blackwell, 1985). Hydrothermal fluids can be redistributed, replenished, or diminished by tectonic events, intrusive/thermal events, or reductions in aquifer porosity due to silicification, argillization, or zeolitization (Bailey et al., 1976; Blackwell, 1985). Evidence of oscillating hydrothermal fluxes exists in evaporite deposits of Searles Lake as elevated concentrations of boron and lithium (Sorey, 1985). Clearly, injections of hydrothermal fluids, similar to the hydrothermal excursion recorded at ~ 3 ka, influence the composition of downstream lakes, and could be responsible for the downward shift in the Nd isotopic composition of chemical sediments in Owens Lake.

No specific hydrothermal anomaly is recorded in temperature profiles or hot-spring deposits at the time when Owens Lake chemical sediments shift to lower values (14-9 ka). However, the current Long Valley Caldera hydrothermal system has been active since ~40 ka, and evidence of a hydrothermal event taking place between ~12 ka and ~7 ka may have been erased by subsequent events. A significant increase in the flux of hydrothermal fluids circulating through young volcanic rocks in Long Valley Caldera should decrease the Sr isotopic composition of the streams receiving hydrothermal discharge as they flow across the caldera floor. Moreover, as previously stated, hydrothermal activity and weathering of Paleozoic metasedimentary roof pendants in the Owens Lake drainage basin govern the Sr budget, so any significant variation in the hydrothermal flux should be recorded in the Sr isotopic record of Owens Lake chemical sediments. However, over the past ~25 ka these sediments show no sign

of such an event, remaining relatively constant at 0.709. This Sr isotopic evidence argues against the hydrothermally-driven isotopic shift in Owens Lake at ~12 ka.

### *5.1.3 Mineral weathering*

Products of chemical weathering reactions on mineral surfaces are the ultimate source of REE in eastern Sierran streams. Therefore, the REE concentration and isotopic composition of Owens Lake water is dependant on the nature of the minerals present in rocks at the headwaters of the drainage basin. Gromet and Silver (1983) quantified the distribution of REE comprising minerals of a granodiorite from the Peninsular Ranges batholith (PRB) of southern California. The PRB formed from the same magmatic arc which produced the Sierra Nevada batholith (SNB), and is essentially a southern extension of the SNB displaced by Late Tertiary tectonism (see section 2.1.1). Therefore, the REE distribution in rocks of the PRB should be similar to the REE distribution in rocks of the SNB.

The most abundant minerals in granitic rocks have been shown to contain the lowest concentrations of REE (Gromet and Silver, 1983). Plagioclase, biotite, and K-feldspar combined account for less than 5% of the REE (except europium) present in the whole rock sample of granodiorite from the PRB (Gromet and Silver, 1983). Hornblende in these rocks can account for up to 15% of the HREE, but all remaining REE (80 - 95%) are contained in the accessory minerals, sphene and allanite (Gromet and Silver, 1983). A theoretical, present-day shift in  $\epsilon_{Nd}$  from the initial value among minerals in the granodiorite can be calculated based on their Sm/Nd ratio and age (Table 7). Upon emplacement, the granodiorite is isotopically homogenous and the  $\epsilon_{Nd}$  value of each individual mineral would be equal. However, each mineral will evolve a unique  $\epsilon_{Nd}$  value over time based on its Sm/Nd ratio (Figure 16). No correlation exists between the concentration of Nd and the calculated present-day  $\epsilon_{Nd}$  value of the minerals present in the

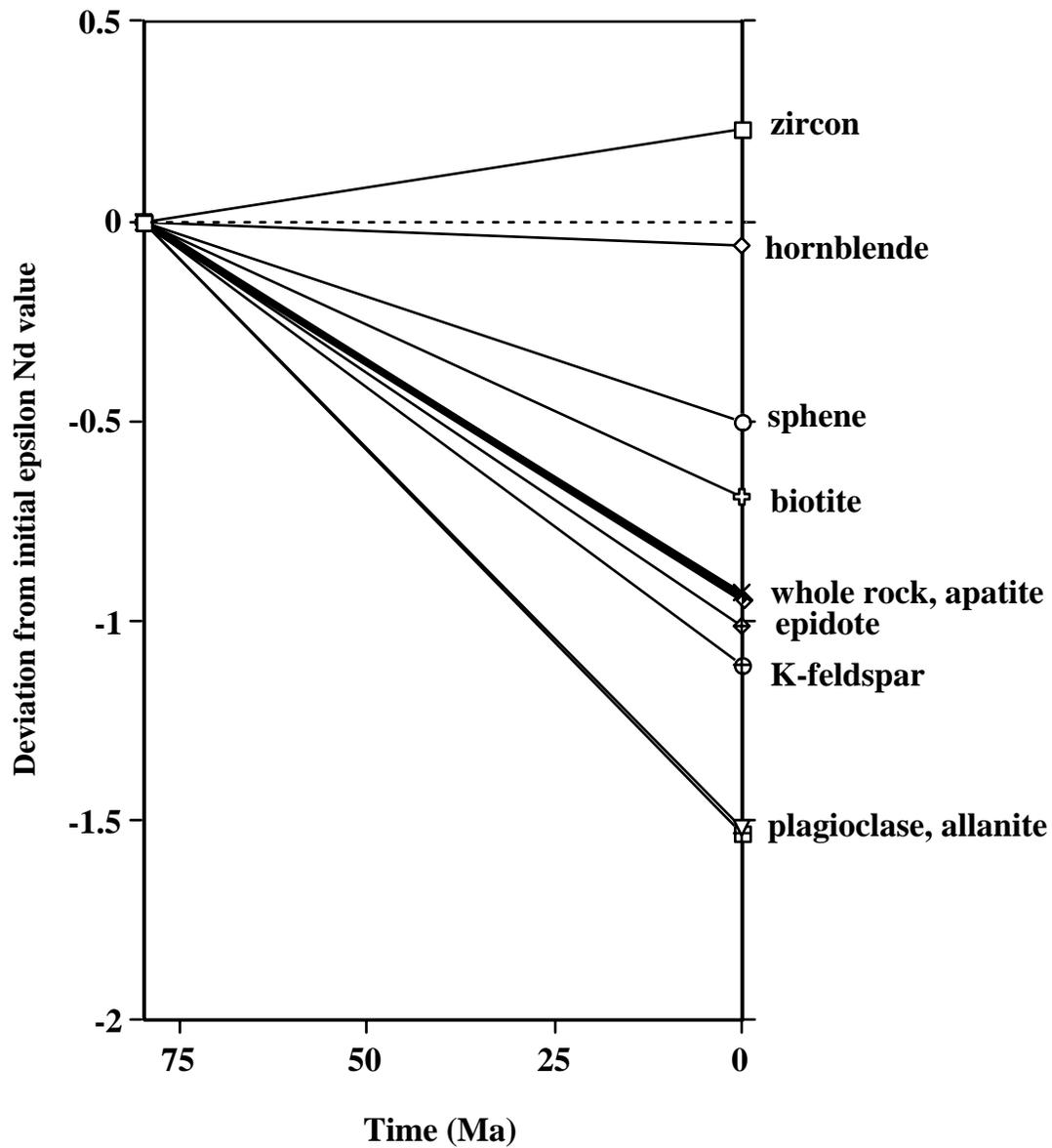
**Table 7.** Theoretical values of  $\epsilon_{Nd}$  based on Sm/Nd values reported for a granodiorite of the Peninsular Ranges batholith by Gromet and Silver (1983). Minerals were assumed to have formed 80 Ma ago with an initial  $\epsilon_{Nd}=0$ . (--) indicates datum is not applicable.

mineral	mineral formula *	modal analysis (wt. %)	[Nd] (ppm)	[Sm] (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$\epsilon_{Nd}^{\dagger}$
zircon	$\text{ZrSiO}_4$	0.010	14.9	5.4	0.2193	0.23
hornblende	$(\text{Ca,Na})_{2-3}(\text{Mg,Fe,Al})_5\text{-Si}_6(\text{Si,Al})_2\text{O}_{22}(\text{OH})_2$	4.82	27.5	8.67	0.1907	-0.06
sphene	$\text{CaTiO}(\text{SiO}_4)$	0.65	2680	655	0.1479	-0.50
biotite	$\text{K}(\text{Mg,Fe})_3(\text{Al}_3\text{SiO}_{10})(\text{OH})_2$	10.9	1.03	0.221	0.1298	-0.69
apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$	0.11	302	52.9	0.1060	-0.93
epidote	$\text{Ca}_2(\text{Al,Fe})\text{Al}_2\text{O}(\text{SiO}_4)\text{-}(\text{SiO}_7)(\text{OH})$	0.52	58.5	9.45	0.0977	-1.01
K-spar	$\text{KAlSi}_3\text{O}_8$	11.2	0.077	0.011	0.0881	-1.11
plagioclase	$(\text{Ca,Na})(\text{Al,Si})_2\text{Si}_2\text{O}_8$	45.6	0.252	0.02	0.0480	-1.52
allanite	$(\text{Ca,Ce})_3(\text{Fe}^{2+},\text{Fe}^{3+})\text{Al}_2\text{O}\text{-}(\text{SiO}_4)(\text{Si}_2\text{O}_7)(\text{OH})$	0.077	16060	1260	0.0475	-1.53
whole rock	-	-	25	4.32	0.1045	-0.94
quartz **	$\text{SiO}_2$	26.1	--	--	--	--

\* from Klein and Hurlbut (1993)

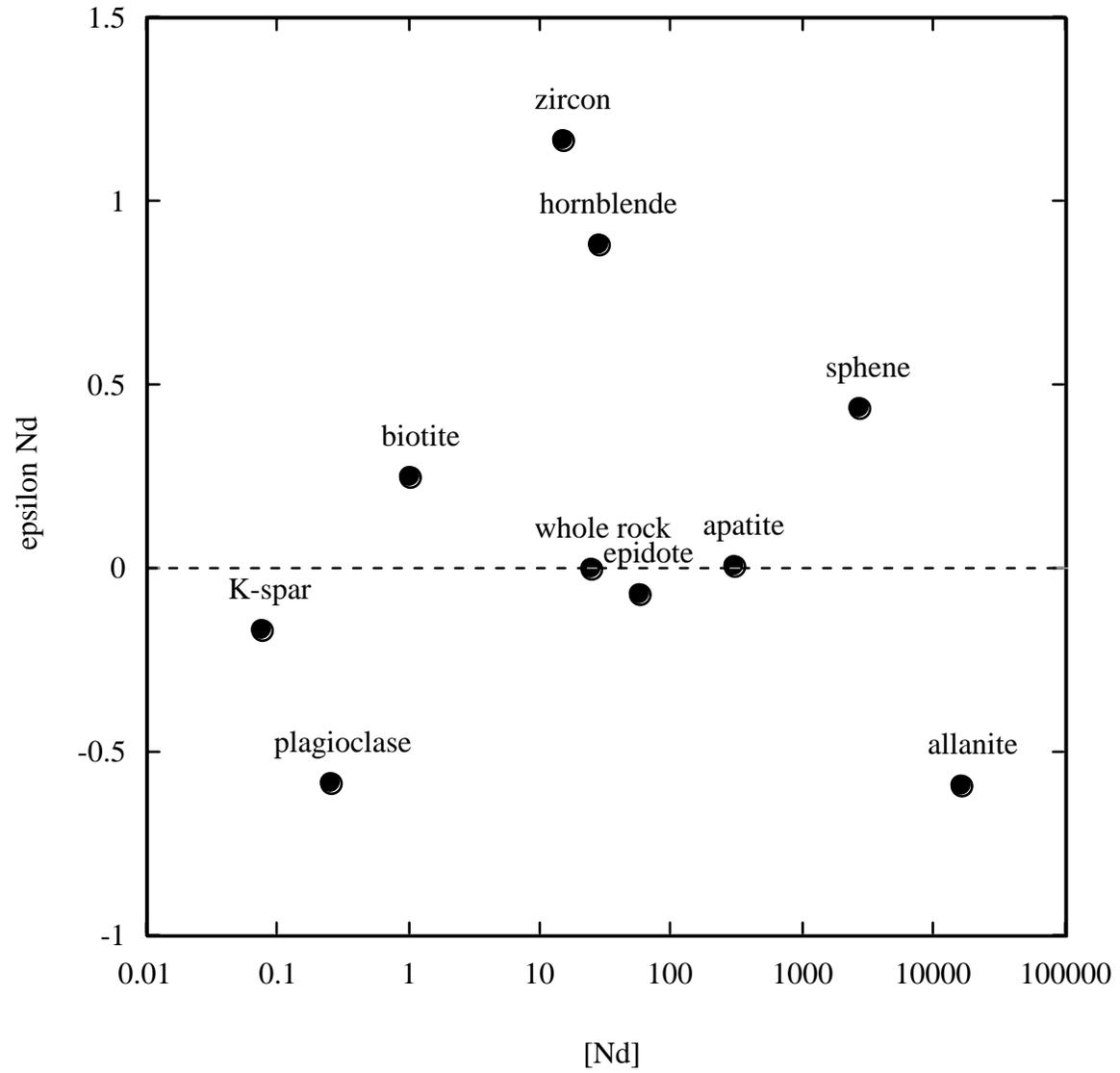
† relative to CHUR = 0.511847

\*\* [Nd], [Sm] in quartz is negligible



**Figure 16.** Deviations of individual minerals in a PRB granodiorite from a shared initial  $\epsilon_{Nd}$  value over time. Minerals evolve a unique  $\epsilon_{Nd}$  value based on their Sm/Nd ratio. Bold line represents the path of the whole rock.

PRB granodiorite (Figure 17). However, when only the common minerals (hornblende, biotite, plagioclase, and K-feldspar) are considered,  $\epsilon_{Nd}$  values increase with the concentration of Nd in the mineral. Therefore, weathering of common minerals could produce a systematic trend in the isotopic composition of their dissolved weathering products. The isotopic composition of the dissolved products of a chemically weathered rock will match that of the remaining whole rock if the minerals weather in proportion to their abundance in the rock. However, preferential weathering of individual (or groups of) minerals will displace the isotopic composition of the dissolved products away from the whole rock value in the direction of the isotopic composition of the weathering minerals. Minerals are not likely to weather in proportion to their abundance because some of the most abundant minerals, such as biotite, hornblende, and plagioclase, are known to be less stable (and more prone to chemical weathering) at surface temperatures and pressures than minerals such as quartz and K-feldspar. After the feldspar minerals, biotite contains lowest amounts of Nd in the PRB granodiorite, and, therefore, its impact on the isotopic composition of weathered mineral products is negligible. Hence, the weathering patterns of plagioclase and hornblende most likely govern the isotopic composition of the dissolved material reaching streams in the eastern Sierras. Hornblende has the highest concentration of Nd among the common minerals in the PRB granodiorite, and can be present in abundances up to 24% of I-type granites in the Sierra Nevada batholith (Ague and Brimhall, 1988). The theoretical  $\epsilon_{Nd}$  value of hornblende in the Peninsular Ranges batholith is nearly 1.5 epsilon units more radiogenic than coexisting plagioclase and allanite (the most Nd-rich mineral in the PRB granodiorite) (Figure 17). Therefore, the shift in  $\epsilon_{Nd}$  values observed in the chemical sediments of Owens Lake at ~12 ka may be caused by a change from a hornblende-dominated mineral weathering regime, to a plagioclase dominated weathering regime. The approximate isotopic



**Figure 17.** Variations in modeled present-day  $\epsilon_{Nd}$  with Nd concentration in minerals from Peninsular Ranges granodiorite. Sample  $\epsilon_{Nd}$  values are normalized to the whole rock value.

composition of the present-day whole rock value for the PRB granodiorite can be determined by summing the relative isotopic composition and Nd concentration of each mineral in the sample:

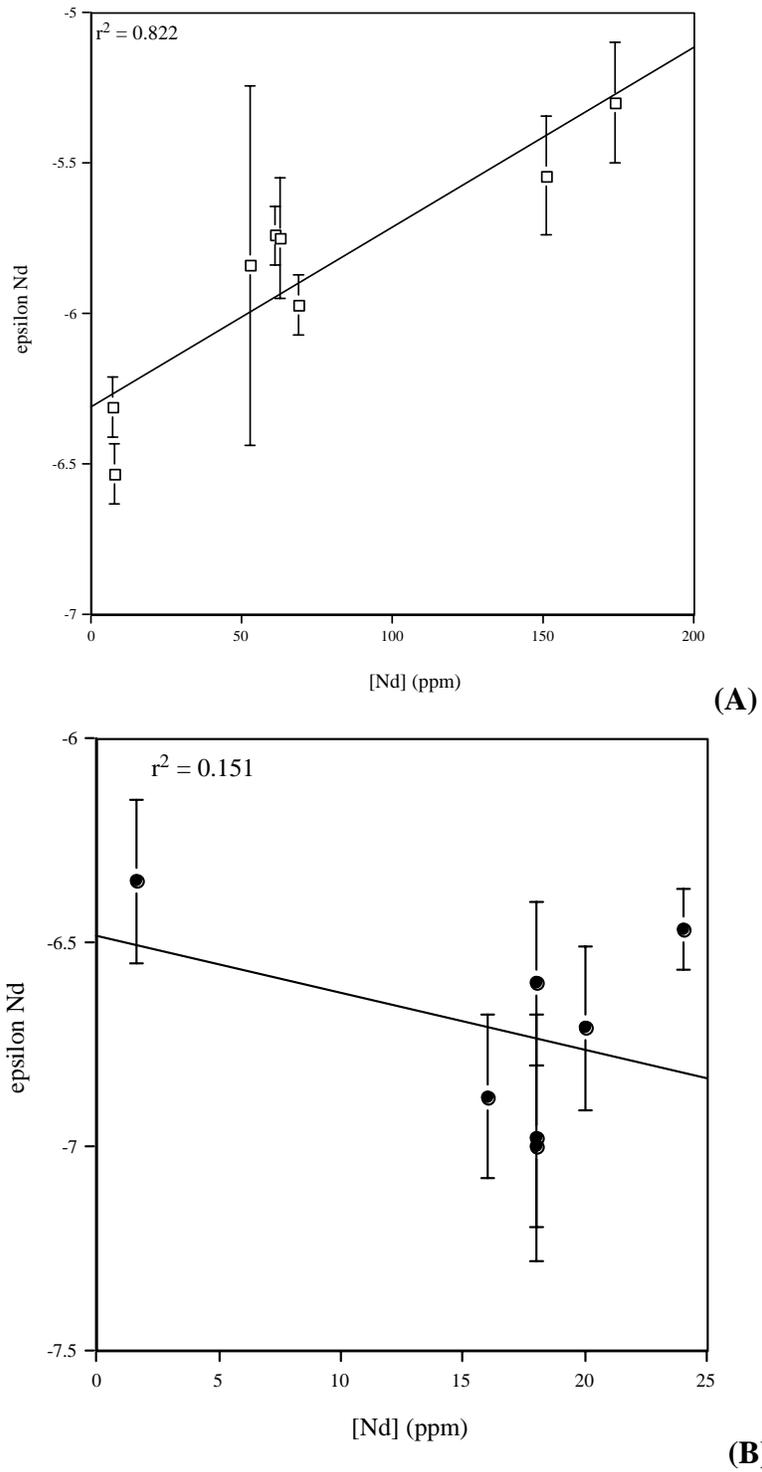
$$\epsilon_{\text{Nd}}^{\text{whole rock}} = \sum_{n=1}^i (\epsilon_{\text{Nd}}^{\text{phase } i}) (f_{\text{phase } i}) \left( \frac{[\text{Nd}]_{\text{phase } i}}{[\text{Nd}]_{\text{whole rock}}} \right) (C_w), \quad (2)$$

where  $f_{\text{phase } i}$  = fraction of phase  $i$  in the rock, and  $C_w$  is the weathering coefficient (from 0 to 1) representing the extent to which a mineral has been weathered. Equation 2 can be used to estimate the  $\epsilon_{\text{Nd}}$  value of the solution ( $\epsilon_{\text{Nd}}^{\text{solution}}$ ) produced by the weathering model by substituting the term  $(1 - C_w)$  for the  $C_w$  term. Equation 2 yields a  $\epsilon_{\text{Nd}}^{\text{whole rock}}$  of -0.89 when no minerals have weathered from the sample. Under a hornblende-dominated weathering regime, when hornblende is the only mineral being weathered out of the sample,  $\epsilon_{\text{Nd}}^{\text{whole rock}}$  increases only slightly to -0.93, while the  $\epsilon_{\text{Nd}}^{\text{solution}}$  acquires the isotopic signature of hornblende (-0.06). Therefore, preferential weathering of hornblende has a relatively minor impact on the Nd isotopic composition of the weathered whole rock residue, but has a significant impact on the Nd isotopic composition of the dissolved weathering products. As hornblende is consumed and the weathering regime begins to favor plagioclase, the  $\epsilon_{\text{Nd}}^{\text{whole rock}}$  remains constant at -0.93 while the  $\epsilon_{\text{Nd}}^{\text{solution}}$  decreases from -0.06 to -0.18. The net effect of the switch from a hornblende- to plagioclase- dominated weathering regime is a downward shift in the isotopic composition of the weathered mineral products. Zircon is a stable, non-reactive mineral, and the remaining accessory minerals do not deviate from the whole rock  $\epsilon_{\text{Nd}}$  composition, so sphene and allanite are likely the only accessory mineral phases capable of producing a significant shift in the Nd isotopic composition of streams draining the eastern Sierras. Some combination of chemically weathering sphene, allanite, hornblende, and plagioclase most likely controls the isotopic composition of these streams; however, the low abundance of the accessory minerals relative to

the major silicate phases favors the hornblende-plagioclase weathering scheme. The positive correlation between  $\epsilon_{Nd}$  and Nd concentration for Owens Lake chemical sediments, and corresponding lack of correlation for Owens Lake clastic sediments supports this idea (Figure 18).

Once the exposed surfaces of rocks are weathered, the isotopic composition of streams in the eastern Sierra Nevada range should stabilize. However, upon the retreat of alpine glaciers in the Owens Lake drainage basin, fresh mineral surfaces are exposed, essentially resetting the chemical weathering scheme in glaciated areas. The last glacial maximum (see section 2.2) in the Sierra Nevada range occurred 25-17 ka ago, approximately 5 thousand years prior to the shift observed in Owens Lake chemical sediments (Bischoff et al., 1997a). This may be a sufficient length of time for the hornblende-plagioclase weathering transition to occur. The glacial-interglacial transition in the eastern Sierra Nevada range is recorded in Owens Lake sediments by variations in clay mineralogy, carbonate abundance, and organic carbon, among other proxies (Figures 3 and 6). During closed-lake conditions, smectite abundance in Owens Lake sediments increases, indicating active chemical weathering processes are taking place in the sediment source areas. Increased weathering in the source region during the onset of the present interglacial period is consistent with an increase in the chemical weathering, and eventually depletion, of hornblende over other, more stable minerals.

A Sr isotopic study of mineral weathering in a soil chronosequence from the western Sierras found K-feldspar to be a significant contributor to the  $^{87}Sr/^{86}Sr$  ratio of the cation exchange pool during the development of young soils, contrary to previous studies which attribute initial fluxes of Sr to biotite during incipient granitoid weathering. (Bullen et al., 1997).



**Figure 18.** Variation in the concentration of Nd with  $\epsilon_{Nd}$  values for the HOAc-leachable (carbonate) fraction (A) and silicate residue (B) of Owens Lake core OL-92 sediments.

Their findings are surprising because K-feldspar is considered resistant to chemical weathering relative to biotite, hornblende, and plagioclase. These authors attribute this weathering discrepancy to differential dissolution of Sr from K-feldspar because it is a trace element, and may behave differently than its stoichiometric counterparts such as K and Na. Similarly, as Nd is a trace element in hornblende and plagioclase, and is nearly absent in biotite, Nd in these minerals may not respond to chemical weathering reactions in the same manner as other coexisting stoichiometric elements.

## 6. SUMMARY AND CONCLUSIONS

Samarium and neodymium are highly enriched in Owens Lake carbonate relative to marine carbonate, indicating strong partitioning of REE into chemical sediments occurs in Owens Lake. Isotopic analysis of Owens Lake sediments indicates dissolved and suspended loads of eastern Sierra Nevada streams have isotopically distinct sources from ~30 to ~12 ka ago. Differences in the isotopic composition of dissolved and suspended loads can be influenced by changing precipitation patterns in the eastern Sierra Nevada range induced by changing atmospheric circulation associated with the last glacial-interglacial transition, by pulses of hydrothermal fluids associated with recent volcanism in the Mono-Inyo volcanic chain injected into Hot Creek in Long Valley Caldera, or by preferential chemical weathering of different mineral phases in the sediment source region of the Owens Lake drainage basin. Differential weathering of hornblende and plagioclase could be responsible for offset in the Nd isotopic composition of Owens Lake chemical sediments from ~30 to ~12 ka ago. The shift in  $\epsilon_{Nd}$  at ~12 ka could reflect depletion of hornblende in the source region in response to increased weathering in the sediment source region.

The Nd isotope system has potential as a paleoclimate proxy in freshwater systems, and can be tested by applying it to older Owens Lake sediments. If this proxy is valid, shifts in the isotopic composition of Owens Lake chemical sediments should occur at all of the major glacial/interglacial boundaries preserved in core OL-92

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