

Effects of Mother Lode-Type Gold Mineralization on $^{187}\text{Os}/^{188}\text{Os}$ and Platinum Group Element Concentrations in Peridotite: Alleghany District, California

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Abstract

Osmium isotope compositions and concentrations of Re, platinum group elements (PGE), and Au were determined for host peridotites (serpentinites and harzburgites) and hydrothermally altered ultramafic wall rocks associated with Mother Lode-type hydrothermal gold-quartz vein mineralization in the Alleghany district, California. The host peridotites have Os isotope compositions and Re, PGE, and Au abundances typical of the upper mantle at their presumed formation age during the late Proterozoic or early Paleozoic. The hydrothermally altered rocks have highly variable initial Os isotope compositions with γ_{Os} values (% deviation of $^{187}\text{Os}/^{188}\text{Os}$ from the chondritic average calculated for the approx. 120 Ma time of mineralization) ranging from -1.4 to -8.3 . The lowest Os isotope compositions are consistent with Re depletion of a chondritic source (e.g., the upper mantle) at ca. 1.6 Ga. Most of the altered samples are enriched in Au and have depleted and fractionated abundances of Re and PGE relative to their precursor peridotites.

Geochemical characteristics of the altered samples suggest that Re and some PGE were variably removed from the ultramafic rocks during the mineralization event. In addition to Re, the Pt and Pd abundances of the most intensely altered rocks appear to have been most affected by mineralization. The ^{187}Os -depleted isotopic compositions of some altered rocks are interpreted to be a result of preferential ^{187}Os loss via destruction of Re-rich phases during the event. For these rocks, Os evidently is not a useful tracer of the mineralizing fluids. The results do, however, provide evidence for differential mobility of these elements, and mobility of ^{187}Os relative to the initial bulk Os isotope composition during hydrothermal metasomatic alteration of ultramafic rocks.

Introduction

GOLD ORES of the Alleghany district in the Sierra Nevada foothills of California are typical of Mother Lode-type, or metamorphic-hosted “orogenic” type, gold-quartz vein deposits worldwide (e.g., Lindgren, 1933; Keays, 1982; Böhlke and Kistler, 1986; Siddiah and Rajamani, 1989; Cox et al., 1991; Groves et al., 1998, 2003; Goldfarb et al., 1998). The origin of the Sierran deposits has been studied using numerous chemical, isotopic, mineralogic, and thermodynamic methods (e.g., Lindgren, 1895; Coveney, 1981; Böhlke and Kistler, 1986; Weir and Kerrick, 1987; Böhlke, 1988, 1989), but the ultimate sources of the hydrothermal fluids and the gold have been difficult to determine (Böhlke, 1999), as they have been in other deposits of this general type (Groves et al., 2003; Goldfarb et al., 2005, and references therein).

Gold is not a product of radioactive decay in nature and it is monoisotopic, so it is impossible to conduct direct genetic tracing of Au using an isotopic system. For some Au ore deposits, the Re-Os isotope system ($^{187}\text{Re} \rightarrow ^{187}\text{Os}$; $\lambda = 1.666 \times 10^{-11}\text{yr}^{-1}$) has proven an effective tracer for dating solution-mobilized Au transport and deposition in associated sulfides (Arne et al., 2001; Brown et al., 2002; Kirk et al., 2002) and assessing the provenance of the Au (Walker et al., 1989a; Hart and Kinloch, 1989; Frei et al., 1998; Kirk et al., 2002; Mathur

et al., 2003). Here we assess the behavior of Os isotopes along with other platinum group elements (PGE) and Au in variably mineralized ultramafic rocks of the Alleghany district. These data are used to determine whether Os and/or other PGE were mobilized during Au ore formation and whether the Os isotopes might yield information about the source of the Au.

Geologic Setting

The major Au-quartz veins of the western Sierra Nevada foothills occur within pervasively metamorphosed, sheared, folded, and faulted rocks of widely varying rock types and ages. In the Alleghany district, diverse host-rock types of mineralized veins range from serpentinitized peridotite to granite, with metamorphic grades ranging from blueschist to amphibolite (Figs. 1, 2). Geochronologic and geologic constraints indicate that the Sierran Au-bearing veins most likely formed after the peak of the regional pervasive deformation of the Nevadan (ca. 155 Ma) compressional event (Böhlke and Kistler, 1986). Dating of minerals associated with the ores by the Rb-Sr and K-Ar methods indicate that Au-bearing veins formed in the Sierra Nevada foothills during the interval of ~ 108 to 144 Ma (Evans and Bowen, 1977; Kistler et al., 1983; Böhlke and Kistler, 1986). The mineralization evidently occurred during a period of active faulting, associated in part with major structural features such as the Melones fault zone (MFZ; Fig. 2). The veins formed from CO_2 -bearing fluids

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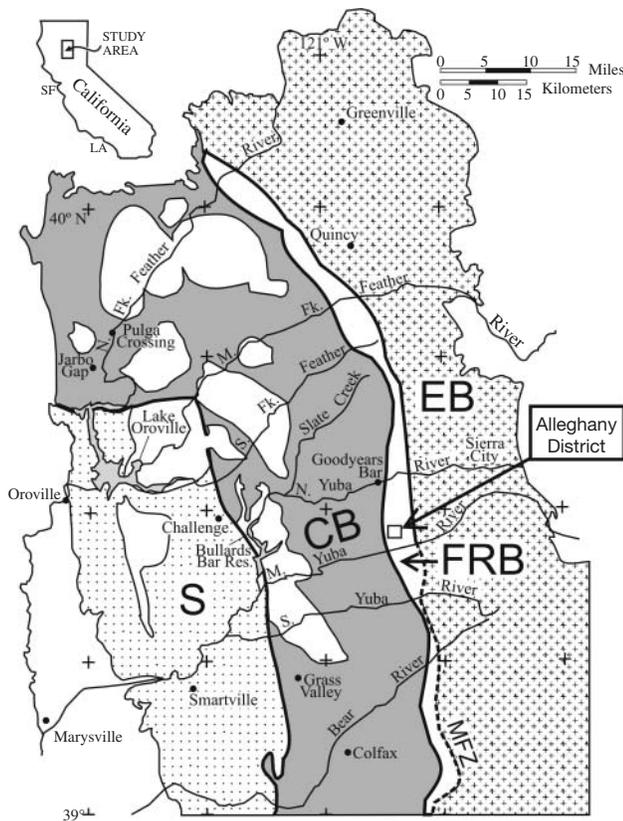


FIG. 1. Geologic map of eastern California. The box shows the area of the Alleghany district enlarged in Figure 2. The four belts shown are the Smartville complex (S), Central belt (CB), Feather River belt (FRB), and the Eastern belt (EB). The Melones fault zone (MFZ) is shown as the dashed line separating the Eastern belt from the Feather River belt. Modified from Day et al. (1985).

that ascended from unknown sources at depth and flowed through fractures in the older igneous and metamorphic host rocks, depositing quartz, gold, and associated minerals, and causing extensive metasomatic alteration of the vein wall rocks. Stable isotope studies, thermodynamic analyses, and fluid-inclusion data indicate the temperatures and pressures during mineralization were within the range of about 250° to 400°C and 1 to 3 kbars, respectively (Coveney, 1981; Böhlke and Kistler, 1986; Weir and Kerrick, 1987; Böhlke, 1989). The fluids responsible for these deposits had low salinities ($Cl \leq 0.2$ molal) with moderately high total carbonate contents ($CO_2 + HCO_3^- \leq 7$ molal) (Coveney, 1981; Böhlke, 1989; Böhlke and Irwin, 1992). Sibson et al. (1988) and Sibson (2007) proposed that veins of this general type represent episodic escape routes for deep fluids trapped near the brittle-ductile transition. Globally, "orogenic" gold-quartz veins appear to be related genetically to compressional tectonics, activation of major fault zones, and deep-seated metamorphism (Groves et al., 1998, 2003; Goldfarb et al., 1998). The deposits at Alleghany apparently formed in a proximal fore-arc setting, following a westward jump in the western North America plate boundary, whereas intrusive magmatic and metamorphic activity occurred to the east and at depth (Böhlke and Kistler, 1986; Weir and Kerrick, 1987).

The Au in the Alleghany district commonly occurs associated with arsenopyrite in quartz veins within or near hydrothermally altered ultramafic rocks. Progressive hydrothermal alteration of the ultramafic host rocks resulted in a series of metasomatic reaction zones, which are referred to by dominant distinctive mineralogy as talc-carbonate, talc-carbonate-quartz, and carbonate-quartz-mica, in order of increasing carbonate content in the direction of the quartz veins (Böhlke, 1989). Other host rocks for mineralization in the district include granite and various metasedimentary and metavolcanic rocks that exhibit varying degrees of carbonate and sulfide metasomatism.

The host peridotites, which occupy premineralization fault zones, are sheared serpentinite with rounded inclusions of massive serpentinite. Precursor rocks were mostly harzburgites (Böhlke, 1986, 1989). Some relatively pristine harzburgites containing relict clinopyroxene and olivine remain in the area. The ages of the ultramafic host rocks are poorly known and could range from at least early Paleozoic to late Jurassic. The peridotites have been interpreted to be parts of a dismembered Paleozoic ophiolite that was tectonically emplaced in the metamorphic sequence prior to the Late Jurassic (Böhlke and McKee, 1984). Earlier studies did not find systematic differences in compositions between the various exposed serpentinite and harzburgite masses in the area other than in the extent of hydration and oxidation during serpentinization (Böhlke, 1989).

Samples and Analysis

The samples analyzed in this study were splits from samples analyzed previously for other constituents (Böhlke, 1986, 1989). Harzburgite samples G6 and 610 and serpentinite sample 517C are representative of the premineralization peridotites. These samples were collected from outcrops several hundred meters from the mineralized veins (Fig. 2). Sample 610 was collected approximately 50 m east of sample G6. The two are from two different blocks of massive harzburgite that are separated and surrounded by a larger mass of sheared serpentinite. Serpentinite sample 487A was also not mineralized but was collected about 10 m from the Gold Crown vein and approximately 60 m along strike from the mineralized Gold Crown samples. Hydrothermally altered samples were collected from intersections of gold-quartz vein faults and host serpentinites in underground mine workings. These samples comprise serpentinites altered to varying extent by hydrothermal fluids associated with the Au mineralization. The serpentinite host at the Gold Crown mine is an extension of the serpentinite sliver that includes outcrop sample 517C (Fig. 2). Field relations and isotopic data indicate that the CO_2 -bearing fluids responsible for Au mineralization were distinct from the fluids responsible for earlier serpentinization of the peridotites (Böhlke and Kistler, 1986).

The chemical separation techniques used in this study for Re-Os isotope analysis and isotope dilution analysis of Ir, Ru, Pt, and Pd have been previously reported by Shirey and Walker (1995), Rehkämper and Halliday (1997), and Becker et al. (2006). Approximately 2 g of very finely powdered whole-rock samples, a mixed spike consisting of ^{185}Re and ^{190}Os , a separate mixed spike consisting of ^{191}Ir , ^{99}Ru , ^{194}Pt , and ^{105}Pd , approximately 4 g of concentrated HNO_3 , and 2 g

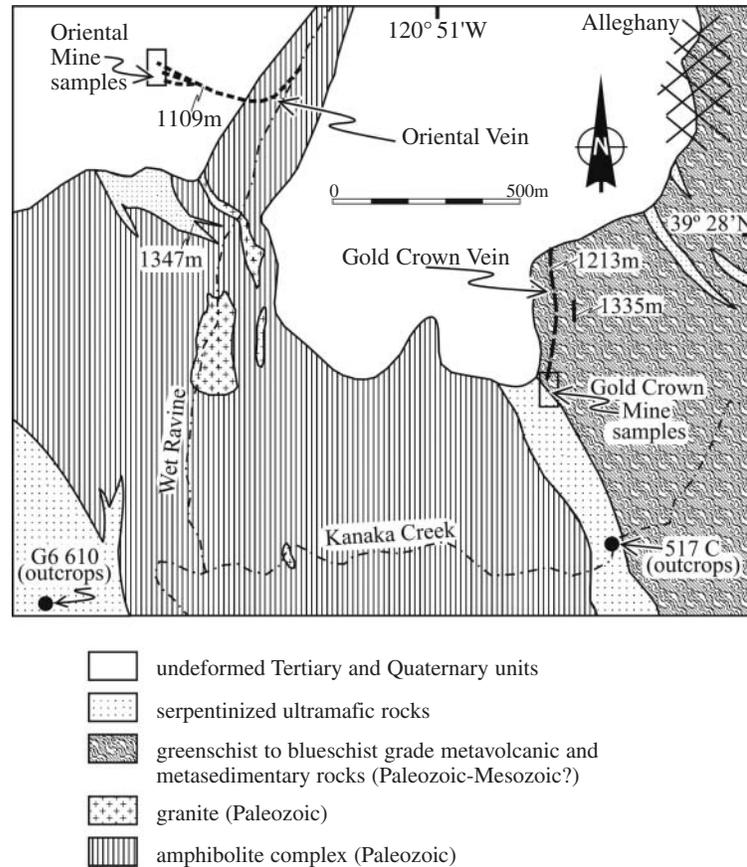


FIG. 2. Detailed map of a portion of the Alleghany district including locations of the Oriental and Gold Crown veins (Böhlke, 1986). Note that the samples of “pristine” harzburgites 610 and G6 are from outcrops in the lower left corner of this map, and serpentinite 517C is from an outcrop south of the Gold Crown mine. The heavy dashed lines and the boxes are vertical projections of the underground veins and underground sampling sites, respectively. The labels in meters indicate the elevations of the underground vein sampling levels and the outcrop elevations of the corresponding veins. Although sample locations appear to be in mixed rock types in these vertical projections, all analyzed samples were entirely from within the boundaries of the ultramafic rock masses at the sample elevations. The cross-hatched area shows the approximate location of the town of Alleghany.

of concentrated HCl g were frozen into Pyrex Carius tubes, sealed and heated in pressurized vessels at 350°C for ≥24 hours to obtain complete sample-spike equilibration. Osmium was purified using a carbon tetrachloride (CCl₄) solvent extraction technique (Cohen and Waters, 1996) followed by microdistillation purification (Birck et al., 1997). The Os total processing blank was 3 ± 2 pg and is inconsequential in all samples.

Rhenium, Ir, Ru, Pt, and Pd were separated and purified from the residual acid using two successive anion exchange columns (200–400 mesh) with resin volumes of 1.0 and 0.2 ml, respectively. The samples were loaded onto columns in 0.8 M HNO₃, then the elements were successively eluted using 6 M HNO₃ (Re and Ru), concentrated HNO₃ (Ir, Pt) and concentrated HCl (Pd). The Re, Ir, Ru, Pt, and Pd blanks for this procedure averaged 2 ± 1, 4 ± 1, 9 ± 3, 300 ± 100, and 60 ± 20 pg, respectively (n = 2). All analyses are blank corrected. Except for Re, blanks comprised <5 percent of the total element analyzed and had minor impact on analytical uncertainties.

Osmium was analyzed via negative thermal ionization mass spectrometry (Creaser et al., 1991). For these levels of Os

(2–5 ng), external reproducibility in the ¹⁸⁷Os/¹⁸⁸Os ratio was about ±0.1% (2σ), based on repeated analyses of comparable quantities of a standard. The analytical uncertainties in the measurement of Os concentrations are estimated to be ≤0.1 percent. Rhenium, Ir, Ru, Pt, and Pd analyses were conducted using a Nu Plasma multicollector inductively coupled plasma mass spectrometer coupled with a Cetac Aridus desolvating nebulizer. All analyses were accomplished using static, multiple Faraday bucket collection. Salient ratios were measured to better than ±0.2 percent (2σ). With the exception of Re, all concentration data are estimated to be accurate and precise to better than ±1 percent. The analytical uncertainty for Re is inversely correlated with its concentration. Uncertainties for samples with 0.2 to 0.3 ng/g Re are ≤±1%, whereas uncertainties for samples with ≤0.05 ng/g ranged from about ±5 to 30 percent.

Accuracy of our laboratory measurements was checked via the measurement of the international UB-N standard (Meisel et al., 2003). Our measurements of UB-N are in agreement with other laboratories at the 1 to 3 percent level (Becker et al., 2006). Although not all minerals are completely dissolved by the Carius tube method, prior studies (e.g., Meisel et al.,

2003) have shown that high-temperature digestion using aqua regia accesses all of the Re and PGE contained in a variety of rock types. Precision was monitored via duplicate aliquants of four sample powders. The duplicates resulted in $^{187}\text{Os}/^{188}\text{Os}$ ratios of ± 0.35 percent or better. Rhenium and Os concentration analyses were in good agreement (all better than $\pm 5\%$). Reproducibility of the other PGE was variable. All PGE data for serpentinite sample 517C were reproducible within ± 2 percent. This defines the analytical limits of our techniques and confirms the precision estimates based on the analysis of the UB-N standard. Variations were greater for duplicate analyses of harzburgite G6 and ore GC22 (as much as 16% difference for Pt in G6 and factor of >2 difference for Pd in GC22). These levels of variation are most likely the result of heterogeneities in the sample powders. The reproducibility of PGE for many peridotitic rocks is often hindered by the fact that PGE are normally concentrated in trace phases that are difficult to homogenize within a sample powder (i.e., the "nugget effect"; e.g., Meisel et al., 2003).

The gold analyses were conducted on ~ 10 percent fractions of the dissolved rock solutions (by volume) taken directly from the Carius tube digestion. Samples were dried several times and ultimately redissolved in 2 mL of 2 percent HNO_3 and centrifuged for 5 minutes at high speed. This supernatant was analyzed using a sector field ICP-MS (Element 2, Thermoelectron Corp.). The absolute concentration of Au in these samples was determined using ^{193}Ir that had <2 percent contribution from the ^{191}Ir spike introduced to the samples prior to Carius tube digestions. The assumed Ir content, as determined by isotope dilution, was used for establishing the absolute concentration of Au in the samples. The Au blank was consistently <30 pg. Error propagation for the Au analyses resulted in an uncertainty of ± 10 percent for all samples.

Results

Concentrations of Os in the host harzburgites and serpentinites are similar to estimates for Earth's primitive upper mantle, a hypothetical mantle reservoir unmodified by crustal recycling or melt depletion-enrichment (Becker et al., 2006; Fig. 3). Rhenium concentrations are lower. This is also reflected in $^{187}\text{Re}/^{188}\text{Os}$ ratios of samples, ranging from 0.218 to 0.293, that are significantly lower than the chondritic average of approximately 0.4. Depleted Re and consequent low Re/Os ratios are common for residues of mantle melting. The harzburgites and serpentinites also have present-day $^{187}\text{Os}/^{188}\text{Os}$ ratios, ranging from 0.1219 to 0.1244, that overlap with or are slightly lower than current estimates for the upper mantle (0.124 to 0.129; Snow and Reisberg, 1995; Walker et al., 2002).

Concentrations of the remaining PGE (Ir, Ru, Pt, and Pd) measured in the harzburgites and serpentinites are within the broad range of concentrations defined by primitive upper mantle and melt-depleted samples of the upper mantle, such as ophiolitic harzburgites and abyssal peridotites (e.g., Walker et al., 1989b; Martin et al., 1991; Snow and Reisberg, 1995; Rehkämper et al., 1999; Meisel et al., 2001; Büchl et al., 2002; Becker et al., 2006; Table 1 and Fig. 4). In contrast, concentrations of Au in all but one of the samples of the harzburgite-serpentinite suite are notably higher than the concentration of ~ 1 ng/g, typical of most mantle peridotites (Lorand et al.,

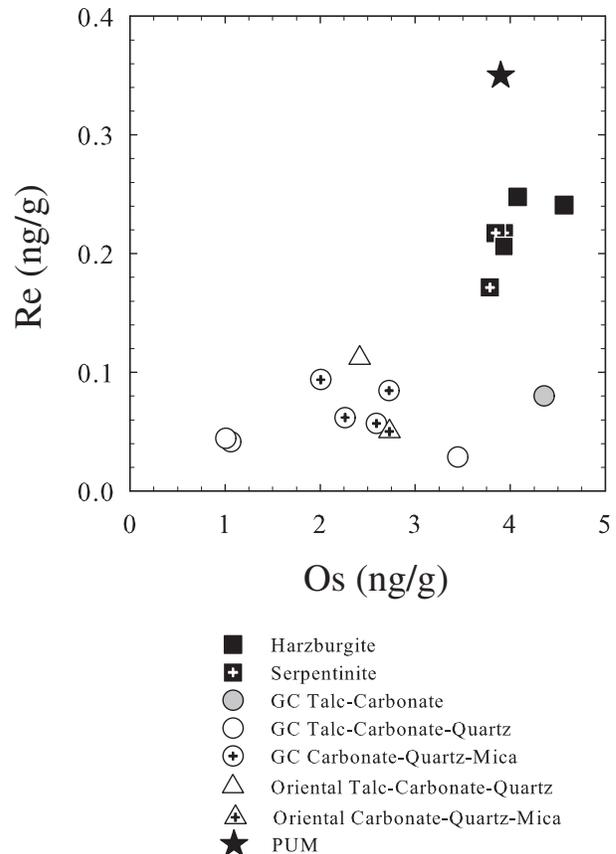


FIG. 3. Concentrations of Re (ng/g) versus Os (ng/g) for altered rocks, serpentinites, and harzburgites. Also shown for reference is the estimate for average upper oceanic mantle (Morgan, 1986). Note that all samples with generally peridotitic compositions, displayed as black squares (harzburgites) and black squares with crosses (serpentinites) have concentrations similar to the upper mantle average. The mineralized samples (open and gray symbols) tend to have substantially lower Re and slightly lower Os concentrations than the other rocks. Data shown include replicate analyses. PUM = primitive upper mantle.

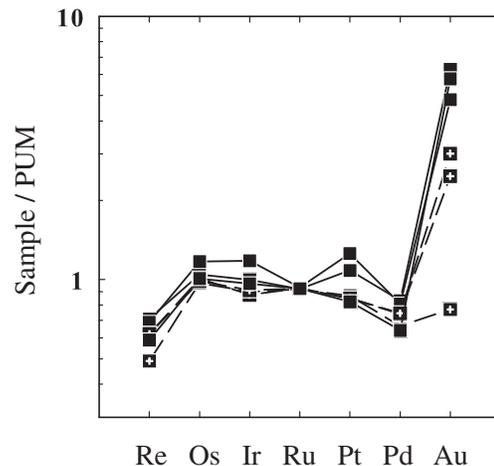


FIG. 4. Abundances of Re + PGE + Au in harzburgites and serpentinites normalized to the primitive upper mantle (PUM) (Re, Os, Ir, Ru, Pt, Pd from Becker et al., 2006; Au from Morgan, 1986). Symbols are the same as in Figure 3.

TABLE 1. Osmium Isotope Compositions and Re, Au, and PGE Abundances

Sample	Rock type	DF	Re	Os	Ir	Ru	Pt	Pd	Au	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Re}/^{188}\text{Os}$	$^{187}\text{Os}/^{188}\text{Os}_{120}$	$\gamma_{\text{Os}(120)}$	T_{RD} (Ga)
<u>Outcrop</u>														
610	Harzburgite	0.95	0.206	3.932	3.374	6.467	6.254	4.550	5.79	0.1222±1	0.252	0.1217	-3.6	0.78
G6	Harzburgite	0.97	0.248	4.076	3.491	6.447	8.223	5.901	6.29	0.1227±1	0.293	0.1221	-3.3	0.73
	Duplicate	0.97	0.241	4.567	4.118	6.525	9.545	5.730	4.83	0.1219±1	0.254	0.1214	-3.8	0.83
517C	Serpentinite	1.00	0.217	3.934	3.059	6.482	6.450	5.242	3.01	0.1241±1	0.266	0.1236	-2.1	0.51
	Duplicate	1.00	0.217	3.845	3.183	6.454	6.299	5.289	2.47	0.1241±1	0.272	0.1236	-2.1	0.51
<u>Gold Crown mine</u>														
487A	Serpentinite	0.98	0.171	3.785	3.145	6.426	6.581	4.716	0.77	0.1225±1	0.218	0.1220	-3.3	0.74
GC13	T-C	1.15	0.080	4.356	3.188	6.892	5.619	4.565	3.26	0.1204±1	0.088	0.1202	-4.8	1.01
GC22	T-C-Q	1.23	0.041	1.060	1.161	1.845	2.480	2.045	3450	0.1203±1	0.188	0.1199	-5.0	1.04
	Duplicate	1.23	0.044	1.007	1.073	1.574	1.777	0.837	2730	0.1205±1	0.213	0.1201	-4.8	1.02
492B	T-C-Q	1.25	0.029	3.447	2.756	5.684	5.384	4.732	73.8	0.1245±1	0.040	0.1244	-1.4	0.39
492BG	C-Q-M	1.54	0.085	2.724	2.281	4.665	4.278	2.976	145	0.1205±1	0.150	0.1202	-4.8	1.01
GC21	C-Q-M	1.28	0.094	2.006	2.011	3.897	3.933	2.994	965	0.1244±1	0.225	0.1239	-1.8	0.46
GC23	C-Q-M	1.58	0.057	2.592	2.217	4.277	3.002	1.893	133	0.1160±1	0.105	0.1158	-8.3	1.65
	Duplicate	1.58	0.062	2.263	1.757	3.973	2.719	1.904	186	0.1164±1	0.132	0.1161	-8.0	1.60
<u>Oriental mine</u>														
583	T-C-Q	1.27	0.112	2.415	2.483	3.927	2.857	3.239	56.7	0.1238±1	0.223	0.1233	-2.3	0.55
611	C-Q-M	1.34	0.050	2.729	2.381	3.935	5.081	2.733	29.3	0.1221±1	0.088	0.1219	-3.4	0.75

Notes: All concentrations are in ng/g; initial $^{187}\text{Os}/^{188}\text{Os}$ ratios and γ_{Os} values are calculated for 120 Ma; γ_{Os} (% deviation from chondritic at time of Au mineralization) and T_{RD} (time of Re depletion model age) are calculated as per Shirey and Walker (1998); hydrothermally altered rocks from each mine are listed in order of increasing carbonate content; complete analyses of these samples are given in Böhlke (1986, 1989)

Abbreviations: DF = dilution factor (see text), T = talc, C = carbonate (magnesite, dolomite), Q = quartz, M = mica (mariposite, a Cr-bearing mica)

1999) and estimated for primitive upper mantle (Morgan, 1986; Fig. 4).

Concentrations of Re and Os in the mineralized samples (with one exception) are lower than in the precursor harzburgites and serpentinites (Fig. 3). Altered rocks have $^{187}\text{Re}/^{188}\text{Os}$ ratios that overlap with the range for the precursor rocks but also extend to much lower ratios. Initial γ_{Os} values (% deviation from chondritic average defined using parameters in Shirey and Walker, 1998) range from -1.8 to -8.3 , calculated for a mineralization age of 120 Ma (Table 1). This age has been estimated for the time of peak mineralization by previous studies (Evans and Bowen, 1977; Kistler et al., 1983; Böhlke and Kistler, 1986). Uncertainty in this age of ± 50 m.y. results in no significant error in calculating the isotopic compositions of these rocks at the time of mineralization because of their low Re/Os ratios. Initial γ_{Os} values are not correlated with either Os or Re concentrations, although all samples with the lowest values are highly mineralized.

Discussion

One of the major objectives of this study is to assess the mobility of Re, PGE, and Au during the mineralization process by comparing their concentrations in rocks that were hydrothermally altered to varying degrees with concentrations in the harzburgites. Serpentinization (hydration), carbonate metasomatism, and quartz veining (associated with Au mineralization) of the ultramafic rocks resulted in substantial dilution of some of the rock-derived elements such that changes in measured concentrations may not always reflect element mobility (Gresens, 1967). To evaluate chemical gains and losses during these processes, Böhlke (1986, 1989) estimated dilution factors (DF) for these rocks based on parallel changes in the concentrations (C) of several relatively immobile elements, including Fe, Mg, Cr, and Ni: $\text{DF} = C_{\text{serp average}}/C_{\text{sample}}$.

Adjusted concentrations of mobile and immobile elements can be calculated to a dilution-free basis by multiplying the measured concentrations in a sample by the mean dilution

factor for the sample given in Table 1. The average serpentinite was assigned a dilution factor of 1; dilution factors for quartz-carbonate rocks derived by hydrothermal alteration of serpentinite are as high as 1.58. This means that the concentrations of elements such as Re or the PGE could be as much as 37 percent lower in a carbonate-altered sample than in a serpentinite precursor, even if those elements were conserved (immobile) during the alteration.

Gains and losses of Re and PGE during hydrothermal alteration are most easily evaluated via plots in which element concentrations are multiplied by the appropriate dilution factor for each rock, then normalized to the precursor rock (i.e., serpentinite). After adjustment for dilution, it is apparent that the concentrations of Re and PGE are substantially lower in most of the mineralized rocks than in the precursor serpentinites or harzburgites, indicating that these elements were removed from the rocks during the hydrothermal alteration (Fig. 5a, b). Removal of elements was evidently not uniform, however, as mineralized samples also have substantially more fractionated patterns compared to the host rocks.

With the exception of talc-carbonate sample GC13, with approximately 3 ng/g Au, all mineralized samples have >29 ng/g Au and are substantially more Au rich than the harzburgites and serpentinites. Samples GC21 and GC22 have ≥ 1 $\mu\text{g/g}$ Au. There is no clear correlation between initial γ_{Os} values and Au concentrations (Fig. 6), although three of the four samples (and replicates) with the lowest initial γ_{Os} values are mineralized samples that also have some of the highest Au concentrations (>100 ng/g).

Origin of Alleghany district peridotites

The Feather River belt, within which the Alleghany district lies, extends for ~ 150 km as a 2- to 20-km-wide zone of largely tectonized ophiolite (Day et al., 1985), structurally separating the Eastern and Central belts in the northern Sierra Nevada area (Fig. 1). The ultramafic rocks of the Alleghany district likely formed as oceanic lithosphere, perhaps

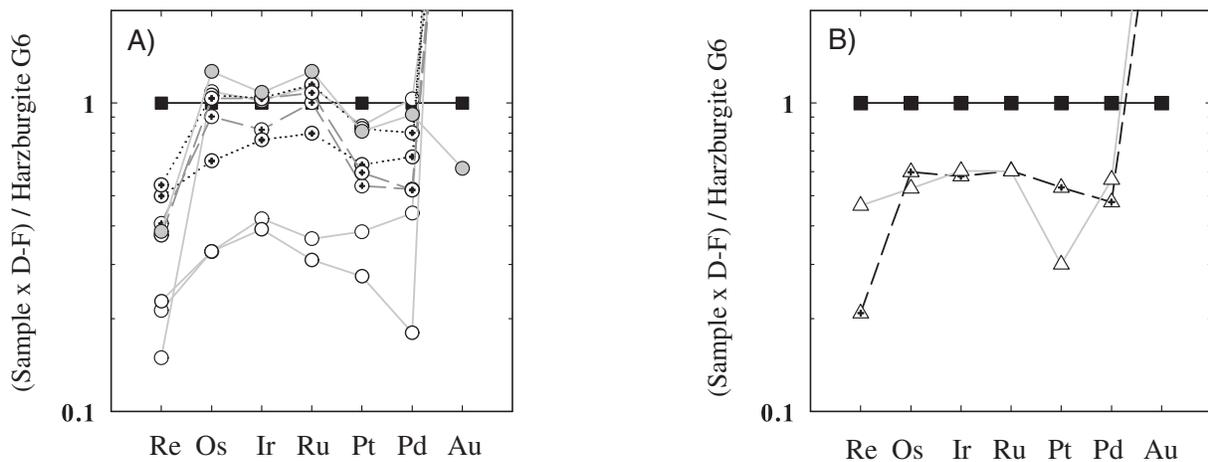


FIG. 5. a-b. Abundances of Re + PGE + Au (abundances multiplied by dilution factors, DF) in altered samples normalized to harzburgite G6 (black squares sample 1 of duplicates in Table 1). Figure 5a shows samples from the Gold Crown mine; Figure 5b shows samples from the Oriental Mine. Note that hydrothermally altered samples are characterized by generally lower concentrations of most elements, except Au, compared to the harzburgite. Gold abundances for most altered samples plot well above the scale of the figure. Symbols are the same as in Figure 3.

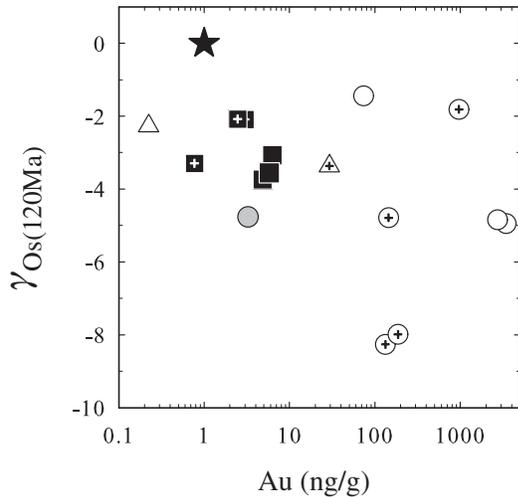


FIG. 6. $\gamma_{Os}(120)$ versus Au concentration, where γ_{Os} is the percent deviation of $^{187}Os/^{188}Os$ from the chondritic average calculated for the approximately 120 Ma time of Au mineralization. Although there is no clear correlation between γ_{Os} and Au, several of the mineralized samples with the highest Au concentrations also have the lowest γ_{Os} values. The gold value for average upper mantle is from Morgan (1986). Symbols are the same as Figure 3.

in a back-arc setting, and were emplaced into Paleozoic and/or older rocks formed at the continental margin. Consistent with this hypothesis, the metamorphic rocks on the eastern side of the Melones fault zone in the Alleghany area include some early to middle Paleozoic continental-margin clastic metasedimentary rocks.

The age of the peridotitic rocks is also poorly constrained. Moores et al. (1999) suggested that the Feather River ophiolitic rocks may have formed during the middle- to late-Paleozoic. Osmium model time of Re depletion ages (T_{RD}) for the Alleghany district peridotites (calculated as per Shirey and Walker, 1998) are conservatively calculated assuming derivation of peridotites from a fertile chondritic source with complete depletion in Re (until the time of mineralization) to yield an Re/Os ratio of zero. The relatively pristine harzburgite samples G6 and 610 give Os T_{RD} model ages of approximately 600 to 700 Ma (Table 1). These data are consistent with a late Proterozoic or early Paleozoic age of melt depletion, although because of variability in the Os isotope composition of the upper mantle, model ages for rocks this young should be considered accurate to no better than about ± 300 Ma (e.g., Reisberg et al., 2004).

Elemental and Re-Os isotope systematics of hydrothermally altered rocks

The host harzburgites and serpentinites show limited variance of Re, PGE, and Au concentrations, and with the exception of Au, concentrations are very similar to mantle-derived peridotites worldwide (e.g., Morgan, 1986; Rehkemper et al., 1999). These observations are consistent with the genetic interpretation of peridotite derived from a dismembered ophiolite.

The altered rocks, in contrast, display a wide range of Re and PGE concentrations, and Os isotope compositions (Figs. 3; 5a, b). One important observation is that there is no

evidence of significant net addition of PGE to any of the altered rocks. They generally have similar or lower abundances of all PGE and Re compared to the unaltered rocks. Further, all of the altered rocks contain Os with subchondritic $^{187}Os/^{188}Os$ calculated for the time of mineralization (all have $\gamma_{Os120} \leq 1.4$). The $^{187}Os/^{188}Os$ of the average upper continental crust was likely >0.5 ($\gamma_{Os120} > +300$) at the time of mineralization, so there is no evidence that the Os contained within these rocks was derived from an evolved upper crustal source.

That the Re and PGE concentrations for most altered samples are lower than the precursor rocks suggests that alteration resulted in a net loss of Re and PGE. Of greatest note is the depletion of Re and lower Re/Os in the altered rocks (Figs. 3, 7a). The unaltered harzburgites and serpentinites were already moderately depleted in Re, at the time of mineralization, relative to the primitive upper mantle. The loss of additional Re during mineralization is consistent with previous studies of ultramafic rocks in which relatively low-grade hydrous metamorphism has been shown to result in significant loss of Re (e.g., Gangopadhyay et al., 2005).

In addition to the low Re/Os ratio, several of the altered rocks have Pt/Ir and Pd/Ir ratios that are lower than any of the unaltered rocks (Fig. 7b, c), and three of the four mineralized samples with the lowest initial γ_{Os} values (GC22, GC23, GC13) have lower Pt/Ir than the host rocks (Fig. 7d). The Ru/Ir ratios of the altered rocks extend both above and below the range of ratios defined by the unaltered rocks (Fig. 7c), so these two elements do not appear to have been fractionated in a consistent manner by the alteration process.

Given the well-documented loss of Re via fluid mobilization in other ultramafic rocks (but evidently not in the Alleghany harzburgite and serpentinite precursors), it seems likely that Re depletion occurred at the time of Au mineralization as a consequence of simple net loss. The relatively undisturbed PGE pattern for the talc-carbonate (magnesite) sample GC13 indicates that relatively modest losses of the PGE prevailed in the more distal alteration zones (farthest from the main fluid-flow paths). The trend toward lower Pt/Ir and Pd/Ir in some of the mineralized rocks could also be interpreted as a somewhat greater tendency toward loss of Pt and Pd relative to Ir, Os, and Ru during the mineralizing event. This interpretation is plausible because in peridotitic rocks, Pt and Pd, and possibly Re, may be hosted by different phases compared to Os, Ir, and Ru (Walker et al., 1996; Luget et al., 2001; Bockrath et al., 2004). Preferential dissolution of a Pt- and Pd-rich phase, such as pentlandite, compared with the Os-Ir-Ru alloys that commonly host these elements in peridotitic rocks (Stockman and Hlava, 1984; Tarkian and Prichard, 1987), could lead to selective loss of Pt and Pd. This conclusion is consistent with the petrologic observation that pentlandite, along with other phases in the harzburgite-serpentinite host rocks, were largely replaced during the hydrothermal alteration that formed the carbonate-bearing mineral assemblages (Böhlke, 1986; 1989). Pyrite, millerite, gersdorffite, and arsenopyrite are the major sulfide phases in the altered samples. We conclude that the Re + PGE concentrations of these rocks were altered mainly by variable dissolution and removal during the metasomatic process.

If the metasomatic process was one of net loss for the PGE, the Os isotope compositions of the altered rocks might be

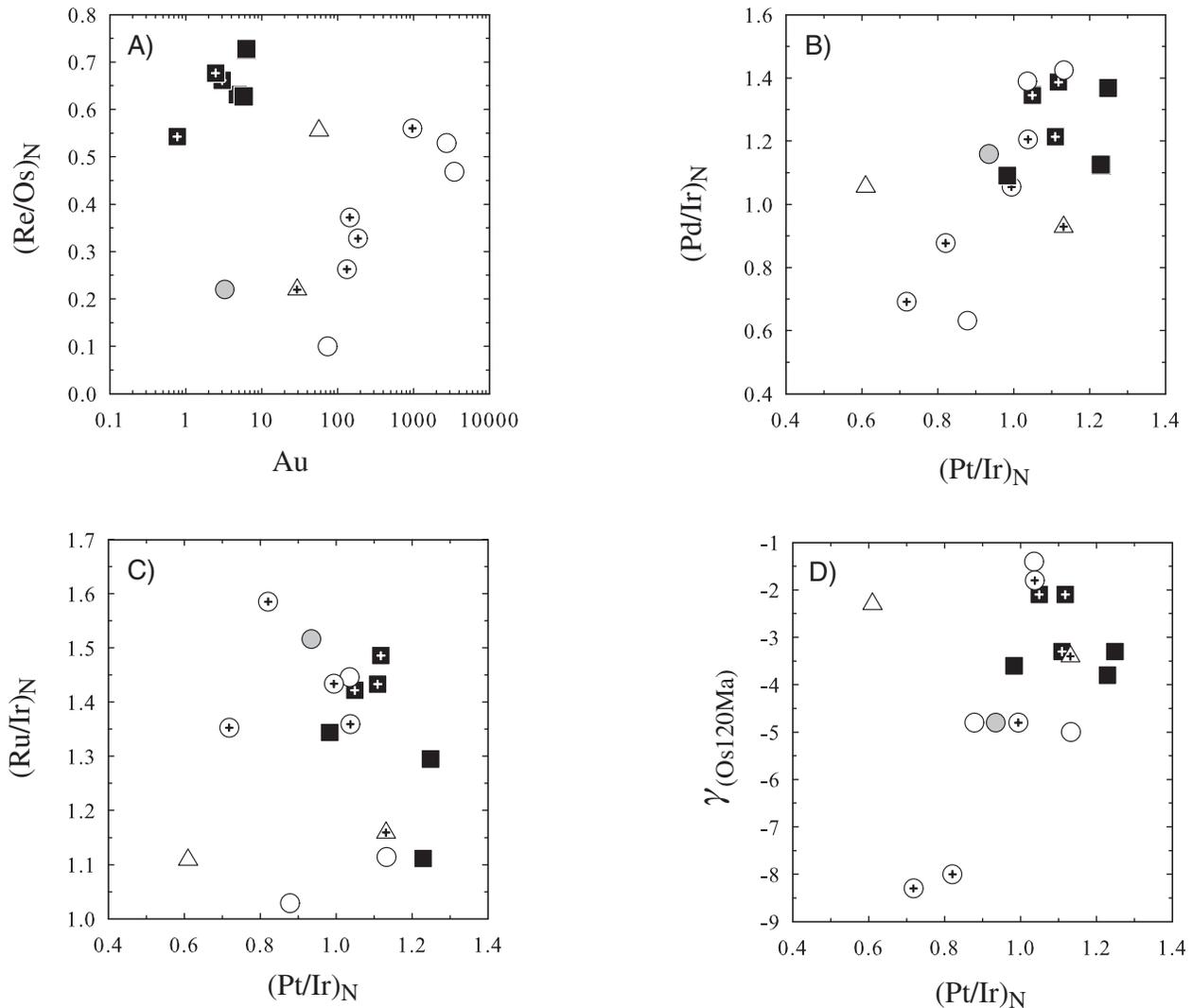


FIG. 7. a-c. Elemental ratio comparisons for hydrothermally altered and unaltered samples. Elemental ratios are normalized (as designated by the subscript N) to values for average primitive upper mantle (PUM) taken from Becker et al. (2006). Figure 7d shows $\gamma_{Os}(120Ma)$ versus $(Pt/Ir)_N$. Symbols are the same as Figure 3.

expected to reflect those of the host rocks at the time of mineralization, not the mineralizing fluid. The initial γ_{Os} values of approximately half of the altered samples plot within the range of compositions defined by the host rocks. Four of the altered samples, however, have significantly lower initial $^{187}Os/^{188}Os$ than the host rocks. One possible explanation of the low γ_{Os} values is that the Os contained within these rocks was partially derived from mineralizing fluids transporting Os with $^{187}Os/^{188}Os$ that was substantially lower than the host rocks. GC23 is the most highly altered of the samples that were analyzed, based on mineralogy and carbonate content. It has a very low γ_{Os} value that is consistent with a minimum time of Re depletion (T_{RD}) model age (Shirey and Walker, 1998) of ~ 1.6 Ga. A hypothetical source for this Os would need to have been removed from the oceanic upper mantle and to have developed a very low Re/Os ratio during the middle Proterozoic to retain this composition. Few rocks residing in the continental crust meet the combined age requirement

and the necessity of long-term low Re/Os ratio, and none are known within the region. We consider this possibility to be unlikely and conclude that the Os present in the altered samples originated in the precursor peridotites and was not added in significant quantities into the rocks by the Au-bearing solutions. Thus, for this system, Os does not appear to be a useful tracer of the mineralizing fluid.

The observation that some of the altered rocks have $^{187}Os/^{188}Os$ ratios that are lower than the presumed ambient mantle at the time of mineralization, but that none of the harzburgite and serpentinite samples are nearly as depleted, may simply be a coincidence of the limited number of samples analyzed. The altered samples containing isotopically depleted Os may have had low $^{187}Os/^{188}Os$ prior to the mineralizing event. Thus, the isotopic heterogeneity could reflect heterogeneity in the precursor peridotite. This is plausible given that some studies of relatively young mantle peridotites have shown that individual rocks within a lithologic unit can

have Os isotopic compositions that vary over a similar range to that observed for the Alleghany ores (e.g., Parkinson et al., 1998; Reisberg et al., 2004; Harvey et al., 2006).

A more likely cause of the depletion in $^{187}\text{Os}/^{188}\text{Os}$ of altered rocks is selective loss of ^{187}Os accompanying the loss of Re at the time of mineralization. The $^{187}\text{Os}/^{188}\text{Os}$ ratios of mineral phases present in ultramafic rocks, such as abyssal peridotites (Standish et al., 2002; Alard et al., 2005) and ophiolite peridotites (Walker et al., 1996; Meibom et al., 2002), can be even more isotopically heterogeneous than individual ultramafic rocks within a lithologic unit. For example, Alard et al. (2005) documented the presence of two generations of magmatic sulfides in an abyssal peridotite. The “first-stage” sulfides had $^{187}\text{Os}/^{188}\text{Os}$ ratios less than the bulk peridotite. “Second-stage” sulfides, interpreted to have formed during melt percolation through the rock, had higher $^{187}\text{Os}/^{188}\text{Os}$ than the bulk peridotite. The isotopic differences between the phases are the result of the time of formation, the original source of Os contained in the phase, and concentrations of Re and Os in the phase.

In a modern peridotite, retention of low $^{187}\text{Os}/^{188}\text{Os}$ in an Os-rich, Re-poor sulfide or alloy is presumably a reflection of the formation of the phase during an ancient melting event. At that time, the $^{187}\text{Os}/^{188}\text{Os}$ of the phase most likely recorded that of the ambient mantle. The absence of Re in that phase leads to complete retardation of subsequent ^{187}Os production. The isotopic composition can be retained in the phase because it is isolated from Re and Os elsewhere in the rock as a result of the steep concentration gradient between the phase and enclosing silicates (e.g., Meibom et al., 2002).

Sulfides with higher Re/Os ratios (and Pt/Ir and Pd/Ir) than the chondritic ratio can result from melt percolation and sulfide precipitation in peridotites (Büchl et al., 2002; Bockrath et al., 2004). Enriched $^{187}\text{Os}/^{188}\text{Os}$ ratios can be produced in phases with high Re/Os relatively quickly, so the presence of ^{187}Os -enriched phases does not imply an enrichment event long before incorporation of the host rock into the crust. This is in contrast to phases with low $^{187}\text{Os}/^{188}\text{Os}$ that may require a depletion event 1 to 2 Ga prior to the incorporation of the rock in the crust.

We propose that at the time of mineralization, the Alleghany district peridotites contained at least two types of PGE and Re host minerals. One type was rich in Os, Ir, and Ru, and was relatively resistant to dissolution by the mineralizing fluids. This could have been Os, Ir, Ru alloys, which are common in some peridotites. This model requires that at least some of the grains formed during the Proterozoic or Archean and were subsequently isolated to establish the ^{187}Os -depleted compositions. The other type was rich in Re, Pt, and Pd, and would have had a suprachondritic $^{187}\text{Os}/^{188}\text{Os}$ ratio at the time of mineralization. This type was considerably more soluble in the mineralizing fluid than the Os-hosting phase. The documented replacement of pentlandite during mineralization makes it a good candidate for the Re-, Pt- and Pd-rich phase. Thus, a plausible explanation for the ^{187}Os -depleted isotopic compositions is preferential loss of ^{187}Os accompanying the loss of Re, Pt, and Pd during hydrothermal alteration during Au mineralization.

Documenting the loss of Re and PGE during Au mineralization has some important implications. The net loss of Os

from the altered rocks means that, at least for ultramafic host rocks, Os isotopes may not be a viable tracer of mineralizing processes. The putative, preferential removal of Os with a high $^{187}\text{Os}/^{188}\text{Os}$ ratio from the altered rocks means that subsequent deposition of the mobilized Os (and Au) in other rock types could lead to incorrect conclusions regarding the source of the fluids if the Os is used as a tracer. In this case, a radiogenic Os signature in such an ore would be interpreted incorrectly to have been derived from a source with a long-term, high Re/Os ratio, such as average continental crust. The results of this study caution against simple interpretations of Os isotopic composition in ultramafic rocks that have been affected by extensive hydrous alteration. Although Au mineralization appears to have led to net losses of Re and PGE from most altered rocks, only Re was highly affected. For example, a heavily altered rock such as talc-carbonate sample GC13 retained a high proportion of its original PGE budget (>90%). This implies that the PGE abundances of other less altered peridotites, such as abyssal peridotites, may still be used to provide valuable information about their mantle origins.

Conclusions

Comparison of Re and PGE concentrations and Os isotopes between hydrothermally altered (carbonatized) peridotites and unmineralized host harzburgites and serpentinites in the Alleghany district, California, allows assessment of chemical transport and exchange of these elements associated with gold-quartz vein mineralization.

The Os isotope systematics and PGE abundances of the host rocks are relatively uniform in composition and consistent with formation as residues of mantle melting during the late Proterozoic or early Paleozoic. In contrast, the samples that have been hydrothermally altered during Au mineralization display a large range in Os isotope compositions at the time of mineralization at about 120 Ma, ranging from similar to that of the host rocks to having γ_{Os} values as low as -8.3. In addition, almost all altered samples that are enriched in Au are variably depleted in Re and PGE relative to the host peridotites, even when corrected for dilution effects resulting from hydrothermal metasomatism. This most likely is an indication of modest (PGE) to extensive (Re) removal of these elements during the alteration process. There is some evidence that Pt, Pd and especially Re were preferentially removed relative to Os, Ir, and Ru.

There is no evidence in the Os isotope or PGE data for their introduction from evolved crustal sources. We interpret the low $^{187}\text{Os}/^{188}\text{Os}$ ratios in some mineralized samples relative to the host peridotites to be largely a result of preferential removal of a phase or phases with relatively high, long-term Re/Os and $^{187}\text{Os}/^{188}\text{Os}$ at the time of mineralization. These results, combined with petrologic data and the lower Pt and Pd concentrations in the same samples, indicate that pentlandite dissolution may have been an important part of this process.

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