

Hydrothermal Enrichment of Gallium in Zones of Advanced Argillic Alteration—Examples from the Paradise Peak and McDermitt Ore Deposits, Nevada

Chapter C of

Contributions to Industrial-Minerals Research

Bulletin 2209–C

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By James J. Rytuba, David A. John, Andrea Foster, Steven D. Ludington, and Boris Kotlyar

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Hydrothermal Enrichment of Gallium in Zones of Advanced Argillic Alteration—Examples from the Paradise Peak and McDermitt Ore Deposits, Nevada

By James J. Rytuba, David A. John, Andrea Foster, Steven D. Ludington, and Boris Kotlyar

Abstract

Gallium is produced as a byproduct from bauxite and zinc sulfide ores and rarely from primary Ga ores. High Ga contents (>60 ppm) can occur in zones of advanced argillic alteration consisting of alunite±kaolinite±quartz associated with quartz-alunite (high sulfidation Au-Ag) deposits. In a magmatic-hydrothermal environment, the zones of advanced argillic alteration associated with quartz-alunite (high sulfidation) Au-Ag deposits have the highest Ga contents (max 120 ppm). In these Au deposits, Ga is enriched in the zone of alunite±kaolinite alteration and depleted in the zone of quartz-rich alteration within acid-leached rocks. Peripheral zones of argillic alteration have Ga contents and Al/Ga ratios similar to those in unaltered volcanic rocks. The zones of advanced argillic alteration that formed in a steam-heated environment in association with hot-spring-type Hg-Au deposits are not Ga enriched, and residual silicified zones have very low Ga contents. The McDermitt Hg and Paradise Peak Au-Hg deposits, Nev., have zones of advanced argillic alteration that are Ga enriched. At the Paradise Peak Au-Hg deposits, Ga is enriched in the zone of alunite±jarosite alteration that formed in a magmatic-hydrothermal environment. Ga is depleted in the zone of opal±alunite alteration formed in a steam-heated environment, in residual silicified zones formed in a magmatic-hydrothermal environment, and in zones of supergene jarosite alteration. At the McDermitt Hg deposit, Ga is enriched in the zone of alunite±kaolinite alteration below the zone of adularia-quartz alteration that coincides with the Hg ore body. The spatial relation of Ga enrichment to alunite-kaolinite alteration suggests that formation in a magmatic-hydrothermal environment. X-ray-absorption spectra of Ga-enriched samples from the McDermitt Hg deposit are similar to that of gallium sulfate and support the association of Ga enrichment with alunite alteration.

Introduction

The recent increase in demand for gallium has resulted from technological advances that use Ga compounds, such as the arsenide (GaAs) in the molecular-scale coating of silicon computer chips. The primary industrial uses of Ga are in the

production of mobile telephones, laser diodes for fiber-optic telephone systems, semiconductor chips, solar-energy cells, and light-emitting diodes (LEDs). With expanding demand for these products, both traditional and new sources of Ga are of increasing interest.

Primary Ga ores are extremely rare, and Ga production from these sources has been very limited. Ga is primarily produced as a byproduct of Al extraction from bauxite ores that typically contain from 30 to 100 ppm Ga. Ga is also recovered during Zn extraction from sulfide concentrates produced from Zn-rich polymetallic sulfide ores. Recycling of semiconductor scrap is the third major source of Ga. The energy required to extract Ga from bauxite and Zn ores is high, and Ga production from these sources is sensitive to changing costs. The price of semiconductor-grade Ga has ranged from \$1,000/kg in 1965, when it was then as valuable as gold, to a high of \$4,500/kg in 2001, when it was valued at about half the price of gold. More recently, the price of Ga has decreased to \$350–400/kg because of decreasing demand in the technology sector. The United States currently relies on imports of Ga and Ga-containing products to satisfy almost all of its technological needs (Kramer, 2002).

Few studies on the geochemistry of Ga in hydrothermal ore-forming systems have been published. Previous studies have concentrated on the properties of minerals and phases of major importance in the ores that are byproduct sources of Ga, and on Ga extraction from recycled products, such as Ga in aluminum hydroxides, Ga metal, Ga in zinc sulfides, and gallium arsenides. This chapter summarizes information about Ga contents in zones of acid-sulfate alteration associated with hot-spring-type Au-Hg deposits, and in quartz-alunite (high sulfidation) Au-Ag deposits; specifically, we describe the Ga enrichment associated with the Paradise Peak Au-Ag-Hg deposit and the McDermitt Hg deposit, Nev. We discuss the distribution of Ga in relation to the alteration zones within these two deposits and document the phases in which Ga occurs, using X-ray-absorption-spectroscopic analysis of samples from the McDermitt Hg deposit.

Ga Geochemistry of Ore Deposits

Ga has many chemical similarities to Al but is much less abundant, with an average crustal abundance of 19 ppm

(Greenwood and Earnshaw, 1998). The chemical similarities between Ga and Al include a 3+ oxidation state, tetrahedral or octahedral coordination, amphotericity, and similar atomic radius. These properties account for the similar geochemical behavior of both elements. The limited mobility of Al in near-surface environments and the similar behavior of Ga account for the Ga enrichment in bauxite and other ores derived from deeply weathered materials. The acid/base and electronic properties of Ga differ enough from those of Al that under certain geochemical conditions, these elements can be separated in near-surface environments by changes in pH or redox conditions. Ga^{3+} also exhibits chemical similarity to Fe^{3+} .

In hydrothermal deposits, Ga has been reported at relatively high concentrations (0.05 weight percent) in feldspars from a Be/rare-earth-element (REE) deposit in Canada, and it may also occur in other aluminosilicate minerals (Tervek and Fay, 1986). Ga occurs at concentrations below 1 weight percent in jarosite and limonite at the Apex Mine, Utah (Bernstein, 1986). Ga commonly occurs within sphalerite in Zn-enriched ore deposit and is believed to substitute for Zn in the sphalerite structure.

Relatively little is known about the processes that control the geochemical behavior of Ga in igneous rocks. Previous studies have demonstrated that the Al/Ga ratio in various rock types ranges from 10,000 to 40,000 (Tervek and Fay, 1986). The Al/Ga ratio is lower in alkaline igneous rocks and in sedimentary rocks that are residual products of intense weathering (Tervek and Fay, 1986). We evaluated the geochemical behavior of Ga in igneous rocks from plate margins, using the worldwide GEOROC (geochemistry of rocks of the oceans and continents) data base that contains 65,000 major- and trace-element analyses of volcanic rocks (Max Planck Institute, 2002), of which 2,928 analyses from convergent-margin environments are valid for both Ga and Al. The Ga content of these volcanic rocks ranges from 8 to about 30 ppm (fig. 1) and may be much lower in ultramafic rocks because they lack significant amounts of feldspar. The Al/Ga ratio increases with increasing Al content, from about 3,000 to 8,000 (fig. 1). The Al/Ga ratio shows no correlation with increasing SiO_2 content or increasing alkalinity of volcanic rocks, suggesting that petrologic processes that lead to more evolved silicic volcanic rocks do not result in significant Ga enrichment. In contrast, previous studies have reported that peralkaline rocks typically have elevated Ga contents (28–39 ppm; MacDonald and Bailey, 1973), although both the accuracy and precision of these older analyses are questionable. Samples of volcanic, volcanoclastic, and sedimentary rocks from the McDermitt deposit have distinctly lower Al/Ga ratios (approx 200–4,000) and show a weaker negative correlation with Ga (fig. 1), reflecting hydrothermal processes that have introduced and remobilized Ga at the McDermitt Hg deposit, as discussed in detail below.

Ga enrichment in other ore-deposit and rock types indicates the potential for additional types of Ga deposits or ore deposits from which Ga may be produced as a byproduct. These environments of Ga enrichment, which differ substantially in their chemistry, mineralogy, and extent of weathering

or oxidation, include magmatic Ti deposits, REE-containing pegmatites and granites, nepheline syenites, and magnetite in iron phosphate ores (Borisenko, 1993). More recently, Ga enrichment has been recognized in some hot-spring-type Hg deposits. The inactive McDermitt Hg deposit in the Opalite mining district, Nev., has recently been evaluated as a potential source of Ga, and Ga contents as high as several hundred parts per million have been reported (Gold Canyon Resources Inc., 2001). Hot-spring-type Hg deposits are commonly associated with zones of advanced argillic alteration, suggesting that this alteration process may be responsible for the Ga enrichment.

Ga Enrichment in Zones of Advanced Argillic Alteration

High Ga contents can occur in zones of advanced argillic alteration associated with several ore-deposit types, including hot-spring-type Hg, silica-carbonate Hg, hot-spring-type (low sulfidation) Au, and quartz-alunite (high sulfidation) Au-Ag deposits. The advanced-argillic-alteration assemblage typically consists of quartz, alunite, and kaolinite but, depending on the hydrothermal environment of formation, may include pyrophyllite, dickite, diaspore, zunyite, woodhouseite, rutile-anatase, and barite (Hedenquist and others, 2000). In quartz-alunite (high sulfidation) Au-Ag deposits, zones of advanced argillic alteration form from disproportionation of magmatic SO_2 to H_2S and H_2SO_4 during condensation of a magmatic vapor plume (Rye and others, 1992). In hot-spring-type Au-Hg deposits, zones of advanced argillic alteration can form in the near-surface steam-heated environment at and above the water table, where atmospheric oxidation of H_2S released from the hydrothermal fluid generates H_2SO_4 (White and others, 1971). In both environments, the acid condensate leaches most major and minor elements from the host rock, leaving residual silica and forming alunite and kaolinite. In a magmatic-hydrothermal environment, transport of REEs and other elements, such as F, Cl, Ti, and P, leads to the formation of minerals that distinguish this from the steam-heated environment.

The limited data on Ga contents in the zones of advanced argillic alteration associated with several ore-deposit types, based on a review of the literature and data acquired during this study, are summarized in table 1. The highest Ga contents occur in the zones of advanced argillic alteration associated with quartz-alunite (high sulfidation) Au-Ag deposits, locally exceeding 100 ppm. The highest Ga contents are associated with the kaolinite-alunite-alteration assemblage. Very low Ga contents occur in quartz from the vuggy-silica-alteration core in such deposits as at the Ashgrove silica deposit, Wash. (table 1). Low Ga contents occur in the zones of advanced argillic alteration associated with hot-spring-type Hg-Au deposits: generally less than 32 ppm (table 1). The few silica-carbonate Hg deposits with associated zones of acid-sulfate alteration also have low Ga contents: less than 12 ppm (table 1). In the steam-heated environment associated with hot-spring-type

deposits, Ga, along with other major and minor elements, is leached from the host rock by the acid condensate and deposited in zones of alunite-kaolinite alteration. The residual silica, consisting of opal and chalcedony, has very low Ga contents. In a steam-heated environment, the source of Ga in the zones of advanced argillic alteration is what was present in the host rock. This source of Ga is relatively small because the acid leaching zone consists of only a small volume of rock, accounting for the relatively low Ga content in kaolinite and alunite. In the magmatic-hydrothermal environment in which high-sulfidation Au-Ag deposits form, Ga is enriched in zones of kaolinite-alunite alteration but depleted in the vuggy-silica-alteration core, because Ga is leached from the vuggy silica and redeposited in the zone of alunite and kaolinite. The magmatic-hydrothermal fluid and acid leaching of the host rock are both potential sources of Ga and contribute to the Ga enrichment in the zones of kaolinite-alunite alteration.

Two ore deposits that contain zones of advanced argillic alteration enriched in Ga are the Paradise Peak Au-Ag deposit and the McDermitt Hg deposit, both in Nevada. The Paradise

Peak Au-Ag deposit initially was mined for Hg before its recognition as a precious-metal deposit. The McDermitt Hg deposit is the third-largest Hg deposit in North America, and significant amounts of Sb are associated with the deposit. Ga enrichment in these two deposits is discussed in detail below.

Ga at the Paradise Peak Au-Ag-Hg Deposit

Paradise Peak is the site of an early Miocene (18–19 Ma) quartz-alunite (high sulfidation) Au-Ag deposit in west-central Nevada. It was mined between 1986 and 1995 and produced about 1.6 million troy oz Au, more than 24 million troy oz Ag, and more than 914,000 lb Hg from about 24 million t of ore. Paradise Peak consisted of the main Paradise Peak deposit and five smaller satellite deposits (John and others, 1989, 1991; Sillitoe and Lorson, 1994). Samples in this study are from mine exposures and drill holes in the main Paradise Peak deposit, where advanced-argillic-alteration

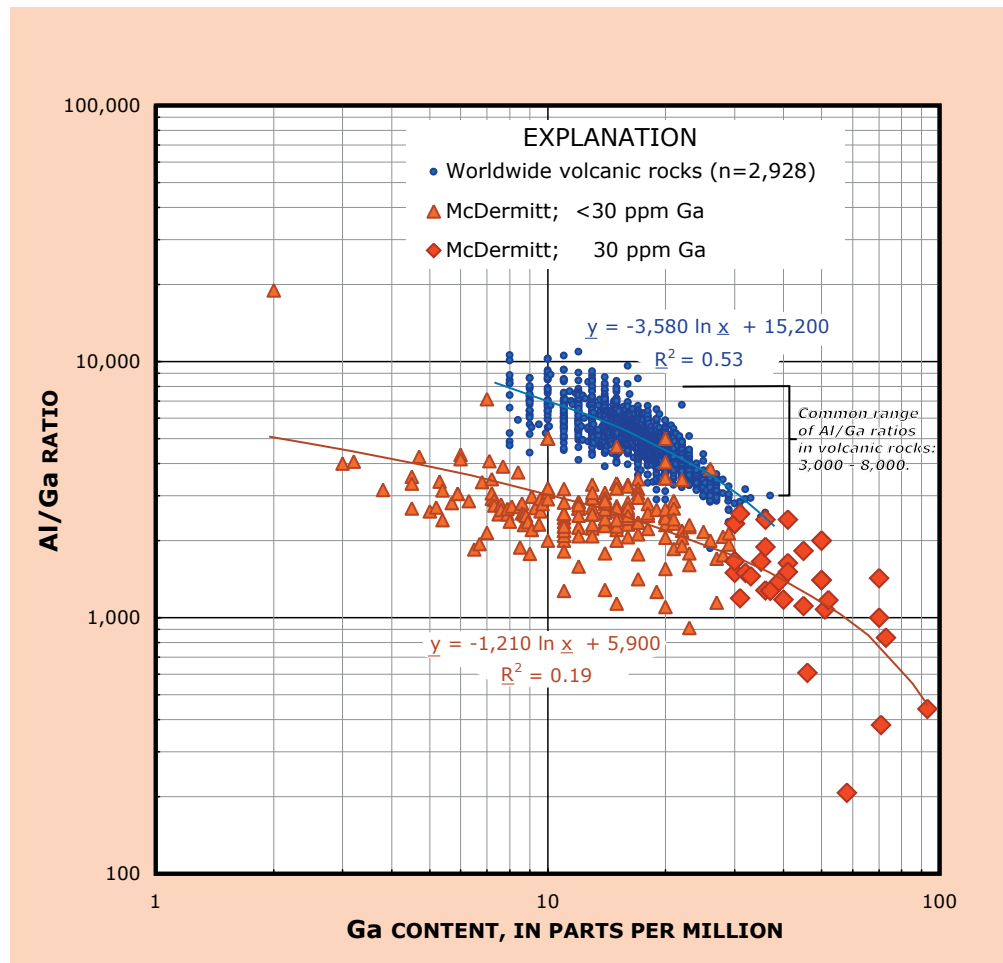


Figure 1. Al/Ga ratio versus Ga content in volcanic rocks from plate margins. Worldwide data base consists of 2,928 volcanic rocks from GEOROC data base (Max Planck Institute, 2002). Volcanic and sedimentary rocks from the McDermitt Hg deposit, Nev., have a lower Al/Ga ratio because of lower Al content of peralkaline volcanic rocks and low-Al smectite clays in sedimentary rocks.

Table 1. Ga content in zones of advanced argillic alteration in various ore-deposit types.

Deposit	Location	Ga content (ppm)	Dominant minerals	Trace elements	Reference
Quartz-alunite (high sulfidation) Au-Ag and silica deposits					
Freedom Flats Au Borealis Mine.	Nevada-----	1–200	Quartz-kaolinite-alunite-hematite	As, Sb, Hg, Tl, Bi, Te, Se, Ba	Eng (1991).
Paradise Peak-----	Nevada-----	84–118	Alunite	Sb, Hg, Tl, Bi, Sn, Ba, Pb	John (1991).
Ashgrove-----	Washington----	<.5 16–101	Quartz-chalcedony Alunite-kaolinite	Cu, As, Bi ---	---
Summitville-----	Colorado-----	19–67	Alunite-kaolinite	Cu, Zn, As	Miller and McHugh (1994).
Hot-spring-type Hg deposits and prospects					
Sulphur Bank-----	California-----	4.0–32	Quartz-kaolinite-alunite-cristobalite	As, Sb, Ba	---
Sulphur Works-----	California-----	4.0–19	Quartz-kaolinite	---	---
McDermitt-----	Nevada-----	2.0–93	Alunite-kaolinite	As, Sb, Zn	---
Hot-spring-type Au-Hg deposits					
McLaughlin-----	California-----	3.0–5.0	Kaolinite-alunite-cristobalite	As, Sb, Hg, Tl	---
Silica-carbonate Hg deposits					
Knoxville-----	California-----	3–12.0	---	Ni, Co, Cr	---
Petray-----	California-----	.3–1.3	---	Ni, Co, Cr	---

assemblages consist of alunite±jarosite, silica-alunite-jarosite, and opal-cristobalite±alunite±jarosite. Other alteration types present include argillic, propylitic, and silicic (John and others, 1991; Sillitoe and Lorson, 1994). Advanced argillic alteration occurs in two distinct zones. The upper zone consists of alunite±jarosite and silica minerals, underlain by silicified rocks (silica minerals with pyrite/marcasite and low-grade Au-Ag) and fringed by a zone of argillic alteration (smectite-pyrite), and a more distal zone of propylitic (smectite-chlorite-pyrite) alteration. The zone of propylitic alteration probably underlies the zone of the silicified rocks, but the Paradise Peak deposit has been displaced from its roots (Sillitoe and Lorson, 1994). The zones of advanced argillic alteration and silicified rocks are cut by several generations of silica-cemented hydrothermal breccia that formed the main Au-Ag ore. Collapse of the hydrothermal system and lower-

ing of the water table resulted in formation of zones of steam-heated acid leaching that formed the second zone of advanced argillic alteration. This alteration occurs along steeply dipping faults and is characterized by residual opal and cristobalite, with minor alunite and jarosite that partly replace the earlier-formed silicified rocks and the zones of alunitic and argillic alteration in the upper parts of the ore body. Most of the native sulfur and cinnabar were deposited during this late-stage acid leaching and advanced argillic alteration.

Mineralogic and sparse fluid inclusion data suggest that the Paradise Peak deposit formed at shallow depths, probably within 200 m of the paleowater table (John and others, 1991; Sillitoe and Lorson, 1994). Most of the main deposit was oxidized during regional detachment faulting that displaced Paradise Peak from its feeder zone. This faulting and supergene oxidation, which occurred about 18–10 Ma (Sillitoe and

Lorson, 1994), was accompanied by the formation of extensive amounts of jarosite and less abundant alunite (Sillitoe and Lorson, 1994; Rye and Alpers, 1997).

Approximately 150 rock samples were collected from active mine faces in 1988–90, and 200 5-ft composite samples were collected from three exploration drill holes through the main Paradise Peak deposit (John and others, 1991; D.A. John and others, unpub. data, 1999). Ga contents were determined by inductively coupled plasma atomic-emission spectroscopy, with a lower limit of detection of 4 or 8 ppm. In addition, 33 samples of unaltered upper Oligocene and lower Miocene volcanic rocks from the Paradise Range that are compositionally similar and age equivalent to the host rocks at Paradise Peak were analyzed for Ga by X-ray-fluorescence or quantitative emission spectroscopy; the data are plotted on figures 2 and 3 and summarized in table 2. Samples were divided into seven groups representing different types of hydrothermal alteration or paragenetic stages (table 2; John and others, 1991; Sillitoe and Lorson, 1994). The division between alunite-, jarosite-, and alunite-jarosite-alteration assemblages is somewhat arbitrary and based on the relative abundances of Al and Fe. Most of the alunite-rich samples and some of the alunite-jarosite samples are believed to represent hypogene-alteration assemblages. The jarosite-rich samples and many of the mixed alunite-jarosite samples probably are supergene.

Observed unaltered volcanic rocks contain 13 to 25 ppm Ga, and most samples contain 15 to 20 ppm Ga (fig. 2). Unoxidized argillically altered rocks have Ga and Al contents similar to those of unaltered rocks. Oxidized samples of argillically altered rocks generally have slightly higher Ga and Al contents than unoxidized samples. Both unaltered and argillically altered rocks plot along the same trend on an Al-versus-Ga diagram (fig. 2), indicating that Ga was not mobilized as a result of the argillic alteration. A positive correlation exists between Ga and Al contents ($r=0.70$ for unoxidized argillic alteration), indicating that Ga is associated with Al-bearing minerals, such as feldspars. Silicified rocks and silica-rich hydrothermal breccias have low Al contents (generally ≤ 0.2 weight percent; John and others, 1991) and Ga contents below the limit of detection (4 or 8 ppm) for all the samples analyzed (fig. 2; table 2).

The Ga contents of samples from the advanced-argillic-alteration zones that contain alunite range from 14 to 118 ppm (fig. 2; table 2). A positive correlation exists between Ga and Al contents, but Ga contents are generally higher at given Al contents than in unaltered or argillically altered rocks. The samples with the highest Ga contents (84 and 118 ppm) were obtained from the upper zone of advanced argillic alteration and occur in pods of friable, fine-grained pink alunite along the southwest side of the deposit near the margins of zones of strong silicification. These samples are similar to alunites that have K-Ar ages and stable-isotopic ratios indicating that they formed from condensation of magmatic gases in a magmatic-hydrothermal environment (John and others, 1989; Rye and Alpers, 1997). Ga contents of mixtures of alunite and jarosite also correlate with Al contents and form a trend similar to that for the more alunite rich samples but markedly different from

the trend for unaltered and argillically altered rocks (fig. 2).

In the lower zone of advanced argillic alteration that consists of acid-leached rocks which formed in a steam-heated environment, most samples of powdery opal±alunite have relatively low Ga and Al contents (fig. 2) and widely varying, but high, Al/Ga ratios (fig. 3). Similarly, samples of jarosite-rich altered rocks that formed during supergene-weathering processes also have low Ga and Al contents and Al/Ga ratios. These samples cluster at the low end of the trend for Ga and Al contents in alunite and alunite-jarosite alteration.

Geochemical and stable-isotopic data from the main Paradise Peak deposit suggest that Ga enrichment is related to the formation of zones of advanced argillic alteration from magmatic-hydrothermal fluids resulting from condensation of magmatic vapor into meteoric ground water (Rye and Alpers, 1997), as commonly occurs in high-sulfidation Au systems in calc-alkaline rocks (Rye and others, 1992). During advanced argillic alteration, introduction of Ga changes the Al/Ga ratio in unaltered rocks, resulting in enrichment of Ga relative to Al. Both Ga and Al were leached from the host rocks during silicification, and the resulting opal-cristobalite rocks have very low Ga contents. Ga may have been transported upward from silicified rocks into the upper zone of alunite alteration, because these altered rock types appear to have formed coevally (John and others, 1991; Sillitoe and Lorson, 1994). Al leached during silicification appears to have been transported out of the zone of ore deposition. Argillic alteration and supergene oxidation of argillically altered rocks appear to affect Ga and Al contents only slightly, other than leaching other cations and S during oxidation, resulting in higher absolute abundances of Ga and Al in the oxidized rocks. Ga and Al contents remain coupled to each other during argillic alteration and supergene oxidation of argillically altered rocks, indicating that Ga substitutes for Al in clay-altered plagioclase and glass where Ga concentration is stabilized. Acid leaching resulting from steam-heated acid-sulfate alteration removes both Ga and Al from argillically and alunitically altered rocks. Al appears to have been preferentially leached, however, because some acid-leached rocks retain relatively high Ga contents despite low Al contents, and Al/Ga ratios are consistently lower in acid-leached rocks than in other altered rock types (fig. 3). Jarosite, of both supergene and possible hypogene origin, appears to act as a dilutant, lowering both Ga and Al contents in proportions similar to their ratio in alunitically altered rocks.

Ga at the McDermitt Hg Deposit

The McDermitt Hg deposit is one of several hot-spring-type Hg deposits and occurrences localized within the McDermitt caldera complex, a Miocene volcanic center consisting of several overlapping and nested collapse structures (fig. 4; Rytuba and McKee, 1984). The volcanic rocks associated with the caldera include peralkaline comendites. Peralkaline rocks typically have relatively low Al contents and somewhat elevated Ga contents, ranging from 28 to 39 ppm

for comendites (MacDonald and Bailey, 1973). The McDermitt Hg ore body is within the caldera and to the northwest of the Cordero Hg ore body, which is localized along a caldera ring fault (fig. 5). The Hg ore bodies are hosted in sedimentary rocks that consist of a silicified basal tuff breccia (opalite) and an overlying lacustrine sequence consisting of tuffaceous sandstone and shale. The sedimentary rocks have been hydrothermally altered, and a systematic alteration zone extends outward from the deposit (Rytuba, 1976). The McDermitt Hg deposit was mined by an open-pit method and produced about 170,000 flasks of Hg; resources of about 200,000 flasks of Hg remain.

The distribution of Ga associated with the McDermitt Hg deposit is based on samples collected from 64 rotary-drill holes used to delineate the Hg ore body (fig. 5). A total of 233 samples were selected from various drill holes to establish the alteration and geochemical zoning within and outside the Hg ore body. Samples consisted of a composite of rock chips from 1.5-m (5 ft) intervals of rotary-drill holes. The alteration mineralogy of each sample was determined by using X-ray

diffraction, and the relative abundance of each mineral by the relative height of diagnostic major X-ray-diffraction peaks for particular minerals. The alteration assemblages present and the range of Ga content in each altered rock type are listed in table 3. Each sample was analyzed for major and minor elements by atomic-emission spectroscopy, and for selected minor elements by atomic-absorption spectroscopy. The resulting data base includes many geochemical and mineralogic variables that are systematically located with respect to the Hg ore body. The three-dimensional geochemical and alteration-mineral distribution for all analyzed elements and minerals was modeled by using the EarthVision software after a logarithmic transformation of the data. The systematic zoning of elements in the deposit is unusual in that in addition to the elements typically present in hot-spring environments (Hg, As, Sb, Tl), elements typically associated with porphyry environments (Mo, Cu, Ti, P, B, F) also display a zoning pattern in the core of the deposit (Kotlyar and Rytuba, 2000). Here, we present the results of this analysis that are relevant to the distribution of Ga associated with the McDermitt Hg deposit.

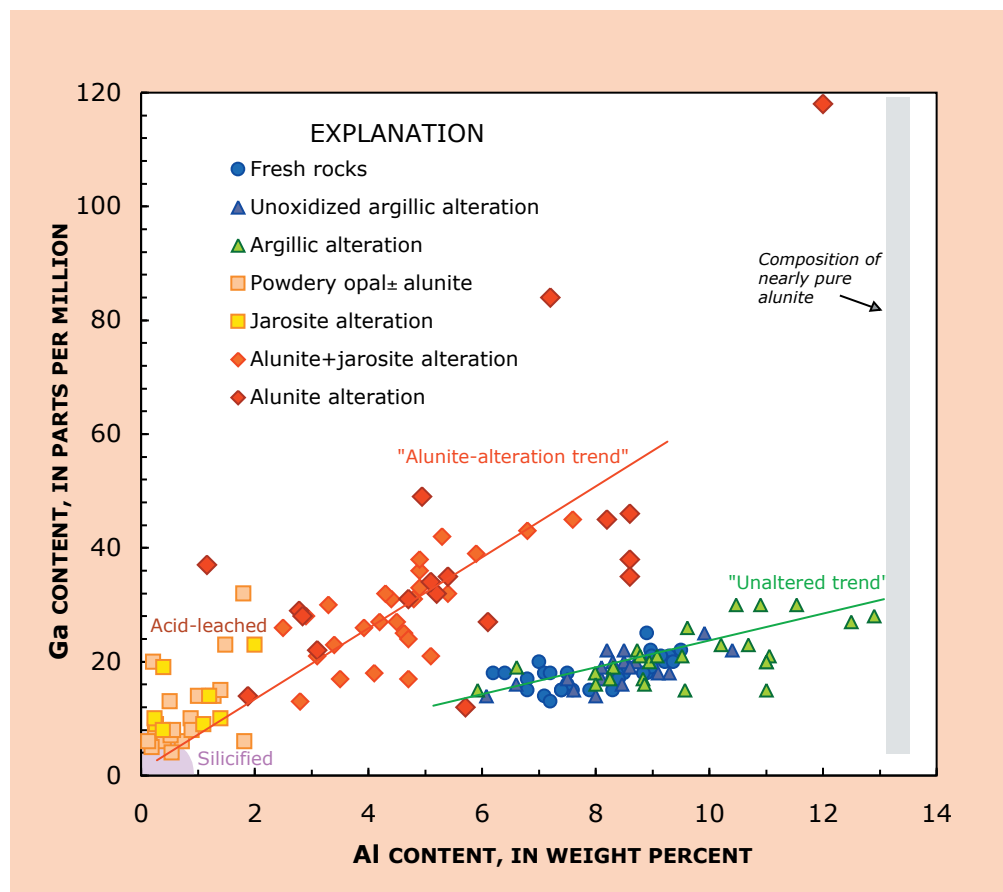


Figure 2. Ga versus Al contents in unaltered volcanic rocks and altered rocks from the Paradise Peak Au deposit, Nev. Volcanic rocks have an Al/Ga ratio that is not changed by argillic alteration. Alunite-bearing rocks in advanced-argillic-alteration zone have highest Ga contents and a distinctive Al/Ga ratio. Ga contents are lower in steam-heated acid-leached rocks. Alunite formed in acid-leached environment has a lower Ga content than alunite formed in magmatic-hydrothermal environment.

Ga in Zones of Advanced Argillic Alteration

The Ga contents in drill-hole samples in and around the McDermitt Hg deposit can be represented by a log-normal distribution (fig. 6). Ga content ranges from 2 to 93 ppm and averages 15 ppm, about the average crustal abundance (19 ppm). Ga exhibits no correlation with most major and minor elements that form the major sulfides and oxides in the ore body, including Hg and Sb, but exhibits a strong correlation with Al (0.73, fig. 7), as well as with some light REEs (La, 0.60; Ce, 0.43). At higher Ga contents (>30 ppm), however, Ga and Al exhibit fewer tendencies to correlate (-0.105), suggesting that Ga is not associated with an Al-bearing phase, such as kaolinite. Total S as sulfide or sulfate was not analyzed, and so the correlation of Ga with sulfide or sulfate phases cannot be evaluated.

The data from the McDermitt Hg deposit can be divided into two populations on the basis of a plot of Al/Ga ratio versus Ga content (fig. 8). Population I comprises samples

with a Ga content of less than 30 ppm and an Al/Ga ratio mostly lower than that for worldwide volcanic rocks, and population II comprises samples with a Ga content of more than 30 ppm and a generally lower Al/Ga ratio (<1,100). Population II includes samples from the zone of advanced argillic alteration that is spatially below the McDermitt Hg ore body, as discussed below. Both populations exhibit the same tendency of increasing Ga content concurrent with a decreasing Al/Ga ratio.

Ga Distribution and Relation to Alteration and the Hg Ore Body

A three-dimensional analysis of Ga contents using the EarthVision software delineates a zone of Ga enrichment where Ga contents exceed 30 ppm (fig. 9). Within this zone of enrichment are two distinct areas where Ga is more strongly enriched and Ga contents locally exceed 60 ppm. The zone of

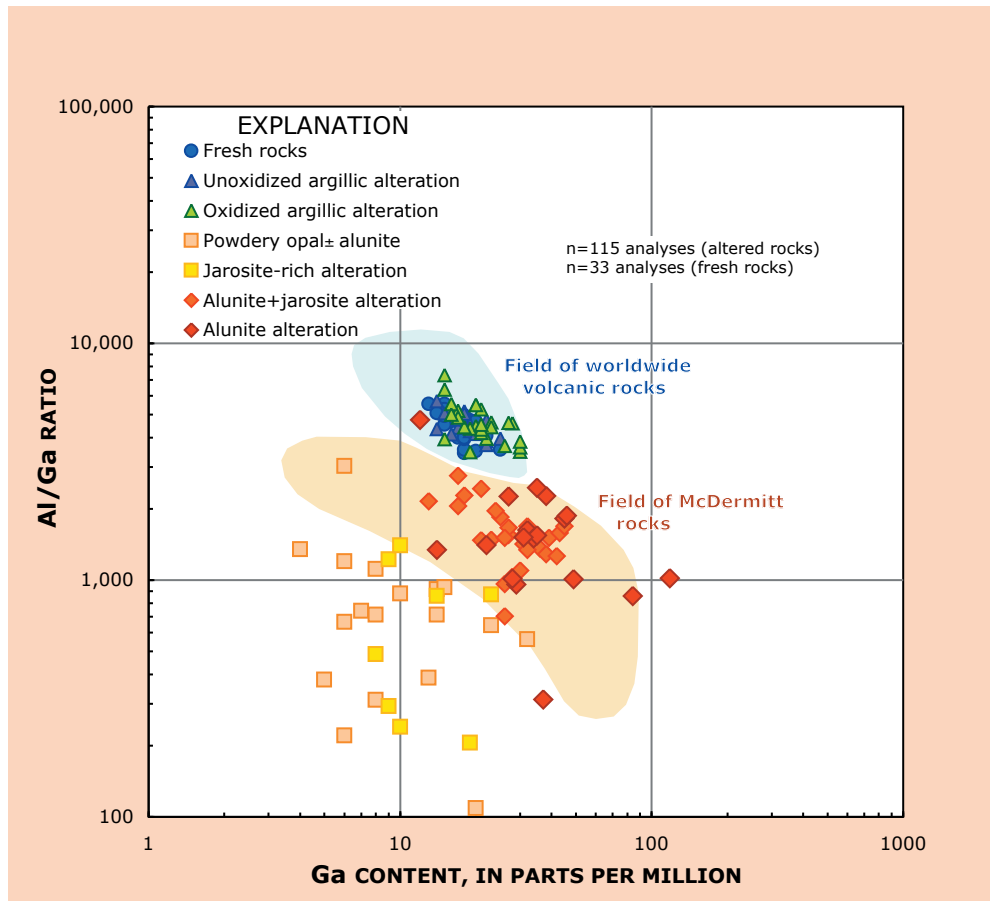


Figure 3. Al/Ga ratio versus Ga content in unaltered volcanic rocks and altered rocks from the Paradise Peak Au deposit, Nev. Unaltered and argillically altered volcanic rocks from Paradise Peak plot within field of worldwide volcanic rocks. Alunite-bearing samples from advanced-argillic-alteration zone at Paradise Peak plot within field of rocks associated with Ga enrichment at the McDermitt Hg deposit, Nev. Opal-alunite and jarosite altered samples from Paradise Peak that formed in steam-heated (acid leached) environment have low Al/Ga ratios and Ga contents.

Table 2. Ga analyses of samples from the Paradise Peak mine, Nev.

Alteration type	Ga content (ppm)	Al/Ga ratio	Number of analyses
Unaltered -----	13–25	3,444–5,538	33
Argillic—unoxidized-----	14–25	3,727–5,714	18
Argillic—oxidized -----	15–30	3,480–7,385	25
Alunite-----	14–118	314–4,758	18
Alunite-jarosite -----	13–42	704–2,765	28
Jarosite-----	8.0–23	206–1,400	8
Acid leached -----	4.0–32	106–3,033	18
Silicification -----	<4–<8	---	~230

Ga enrichment is not exposed at the surface and lies mostly below the Hg ore body (fig. 10). The base of the Ga-enrichment zone is open at depth and so is projected to extend below the depth of the drill holes.

The Hg ore body occurs within a zone of adularia and quartz alteration that extends outward from the Hg ore body and is laterally replaced by a zone of montmorillonite alteration (fig. 10). At increasingly greater distances from the ore body, a zone of zeolite alteration and, farther outward, unaltered glassy tuffaceous sedimentary rocks are present (Rytuba, 1976). Below the ore body is a zone of advanced argillic alteration consisting of kaolinite±alunite±quartz. Factor analysis of the alteration minerals present in the total of 233 samples indicates three alteration assemblages (table 4): (1) a zeolite assemblage composed of clinoptilolite±mordenite that occurs around the northeast periphery of the ore body, (2) a potassic-alteration assemblage composed of adularia±quartz that occurs within the core of the ore body, and (3) an advanced-argillic-alteration assemblage composed of kaolinite±alunite that coincides with the zone of Ga enrichment. Cristobalite has a negative correlation with all three alteration assemblages because the unaltered tuffaceous sedimentary rocks consist of amorphous-glass shards and cristobalite.

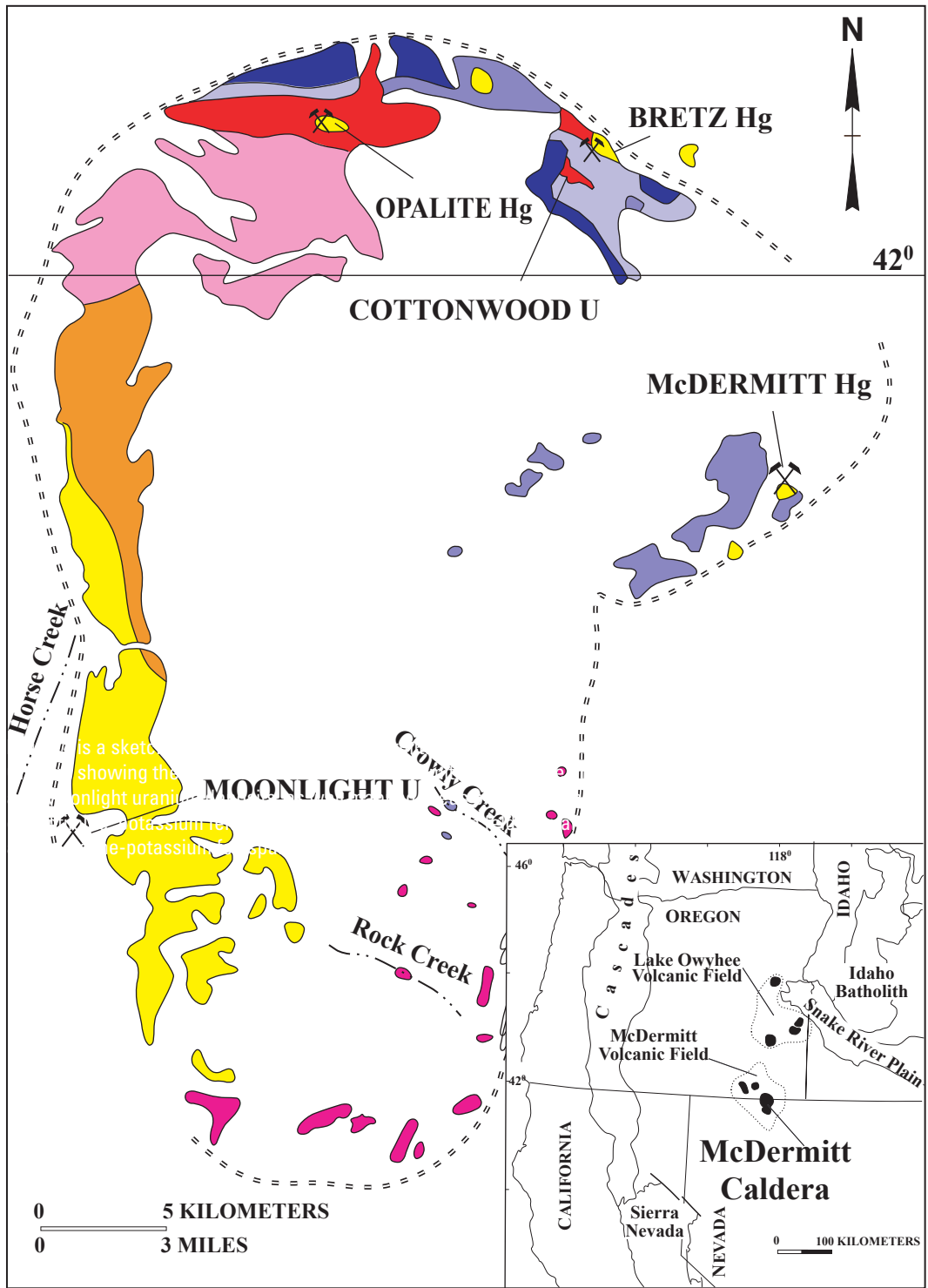
The zone of Ga enrichment primarily occurs within the zone of advanced argillic alteration. In hot-spring-type Hg deposits, the zone of advanced argillic alteration that forms in a steam-heated environment is typically above the zone of adularia alteration, but not at the McDermitt deposit. The position of the zone of advanced argillic alteration and the unusual trace-element zonation (Kotlyar and Rytuba, 2000) suggest that the zone of advanced argillic alteration at the McDermitt Hg deposit formed from a magmatic vapor plume released from a rhyolite intrusion emplaced along the caldera ring-fracture zone. Ga enrichment in this zone of advanced argillic alteration thus appears to have resulted from magmatic-hydrothermal processes that transported and concentrated Ga during alunite-kaolinite alteration. It is unclear from field relations whether the alunite-kaolinite alteration occurred before or after formation of the Hg ore body and thus is unrelated to the Hg deposit. Alternatively, the alteration may represent an early stage of the hydrothermal system

as it evolved from a magmatic-hydrothermal stage to a low-temperature hydrothermal stage that deposited the Hg ore body.

Preliminary Identification of Ga-Enriched Phases

Bulk X-ray-absorption spectroscopy (XAS) at the Stanford Synchrotron Radiation Laboratory was used to identify the minerals and phases in which Ga resides, because the relatively low Ga contents in samples from the zone of advanced argillic alteration precluded the use of other geochemical techniques, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), or microprobe analysis. XAS is an element-specific probe of local molecular structure that can be utilized in both a qualitative/semiquantitative mode (useful for preliminary spectral interpretations, as presented here) and a quantitative mode. Both modes are useful for identifying the most abundant minerals and (or) phases in which Ga resides. Quantitative identification of Ga-bearing phases and minerals by XAS requires further development of a reference library of spectra from known Ga-bearing phases and minerals.

X-ray-absorption fine-structure (XAFS) spectra were collected from commercially available, reagent-grade materials [gallium arsenide (GaAs), gallium oxide (Ga₂O₃), gallium sulfate (Ga₂(SO₄)₃)] and from four alteration-zone samples enriched in Ga from the McDermitt Hg deposit. The XAFS spectrum is typically divided into two parts for presentation and analysis: (1) the X-ray-absorption near-edge-structure (XANES) spectrum and (2) the extended-X-ray-absorption fine-structure (EXAFS) spectrum. As plotted in figure 11 and listed in table 5, the absorption-edge (inflection point) positions of XANES spectra vary as a function of both oxidation state and coordination environment (for Ga, the distinction between octahedral and tetrahedral coordination is especially important). The absorption-edge positions of XANES spectra collected from Ga-enriched samples from the McDermitt Hg deposit (fig. 11) are most similar to that of Ga₂(SO₄)₃, which contains Ga(III) in octahedral coordination. The absorption-edge position of Ga₂O₃ is shifted to a lower energy relative



EXPLANATION

- | | | |
|--|---|--|
| Glass | Clinoptilolite | Analcime-clinoptilolite-K-feldspar |
| Glass-clinoptilolite | K-feldspar | Analcime-K-feldspar |
| Clinoptilolite-mordenite | Clinoptilolite-K-feldspar | |

Figure 4. McDermitt caldera, southeastern Oregon. Hg ore deposits are hosted in caldera-fill sedimentary and volcanic rocks that are altered to zeolite, argillic, advanced argillic, and K-feldspar mineral assemblages as a result of hydrothermal and diagenetic processes.

to $\text{Ga}_2(\text{SO}_4)_3$ because Ga_2O_3 contains both octahedrally and tetrahedrally coordinated Ga(III), and the absorption-edge position of GaAs is shifted lower still because GaAs consists of Ga solely in tetrahedral coordination. These observations suggest that octahedral Ga(III) is the predominant form of Ga in drill-hole samples from the McDermitt Hg deposit.

XANES spectra can also be used for quantitative “fingerprinting” of specific coordination environments by least-squares fitting of model XANES spectra to sample unknowns. The “fingerprints” of the XANES spectra of samples from the McDermitt Hg deposit are similar (but not identical) to the XANES spectrum of $\text{Ga}_2(\text{SO}_4)_3$ (compare spectra in fig. 11).

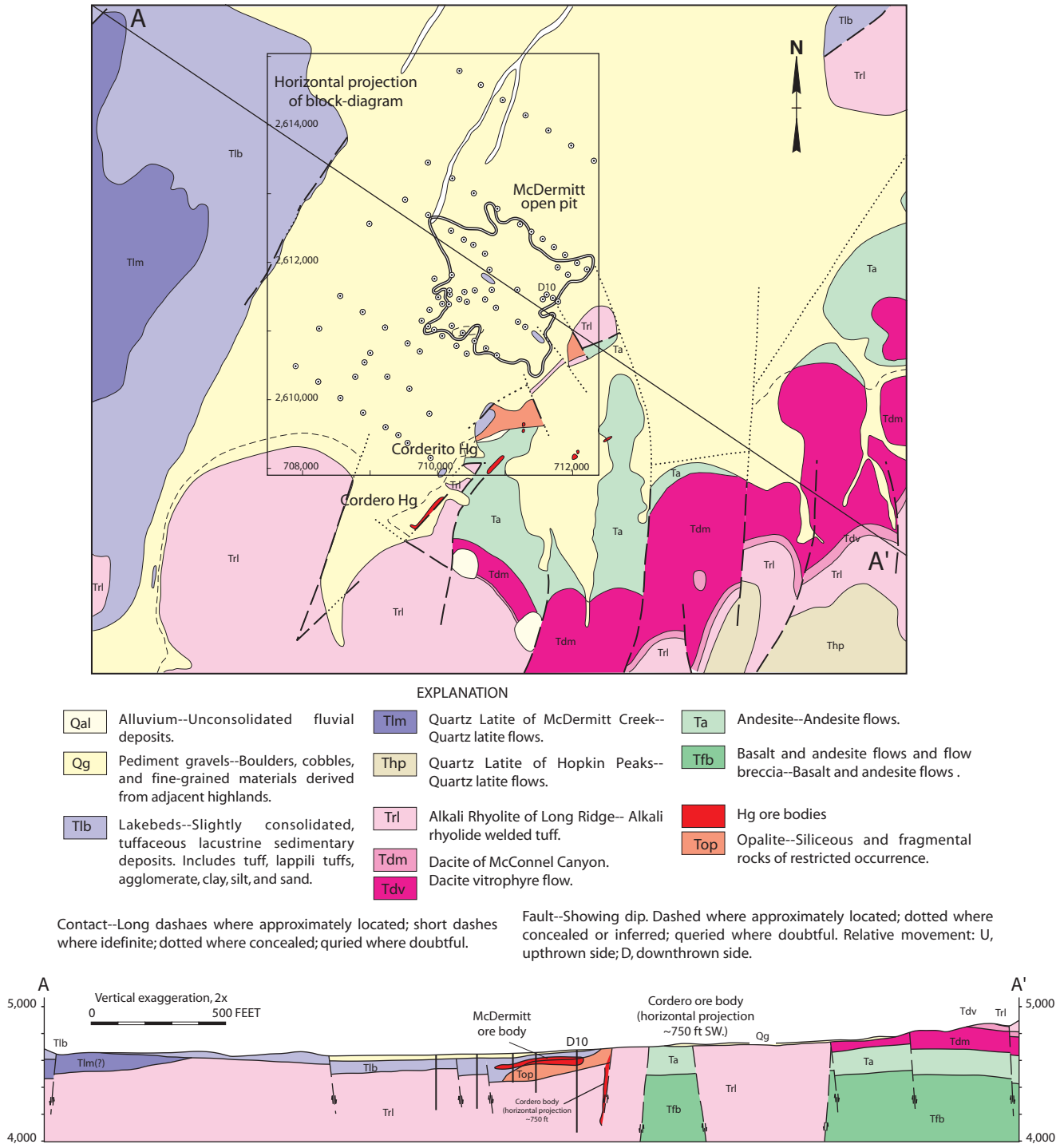


Figure 5. Map and cross section of McDermitt Hg deposit and adjacent area, Nev., showing selected drill holes (circles) used for this study. Square in middle of map is horizontal projection of block diagram in figure 9 showing zone of Ga enrichment (local mine coordinates in feet).

Table 3. Ga analyses of samples from the McDermitt Hg deposit, Nev.

Alteration type	Ga content (ppm)	Al/Ga ratio	Number of analyses
Fresh rock -----	4.5–36.0	1,857–5,000	26
Adularia -----	6.7–50.0	1,148–5,000	23
Alunite+kaolinite+quartz -----	5.3–51.0	1,078–5,000	55
Argillic -----	5.0–93.0	206–3,808	31
Kaolinite+quartz -----	2.0–72.3	835–19,000	61
Silicification -----	4.5–71.0	380–3,333	23
Zeolite -----	3.8–40.0	1,000–7,143	27

Least-squares fits using this model alone as an end member verify what can be observed visually. The Ga XANES spectra for sample AM406–145 (fig. 11B) is most similar to that of $\text{Ga}_2(\text{SO}_4)_3$, whereas the spectra for the other three samples differ considerably (table 5).

EXAFS spectra and derivative Fourier transforms (FTs) of model materials and Ga-enriched samples from the McDermitt Hg deposit are plotted in figure 12. Each EXAFS spectrum is a sum of constructively and destructively interfering sinusoidal frequencies that can be separated by the Fourier transformation. The positions of peaks in the FTs plotted in figures 12B and 12D are too short because they have not been corrected for the identity of the next-nearest-neighbor atoms. The Ga next-nearest-neighbor distances listed in table 5 have been approximately corrected by adding 0.5Å to the radial distances measured from the FTs in figure 12. Similarities between the EXAFS spectra/FTs of $\text{Ga}_2(\text{SO}_4)_3$ and the drill-hole samples

from the McDermitt Hg deposit, coupled with the coincident Ga next-nearest-neighbor interatomic distances listed in table 5, suggest that Ga is hosted predominantly by sulfate minerals, where it is octahedrally coordinated by six oxygen atoms. Octahedral Ga-O distances are approximately 0.6Å longer than tetrahedral Ga-O distances, giving rise to the bifurcated Ga-O FT peaks in the Ga_2O_3 spectra. Similar features suggestive of tetrahedrally coordinated Ga also occur in the FTs of samples AM68–170 and AM34–130 (fig. 12D) but are smallest in the FT of sample AM406–145, which was shown by XANES spectral analysis to have a local coordination environment most similar to that of $\text{Ga}_2(\text{SO}_4)_3$. Either oxide or aluminosilicate minerals could host the tetrahedral Ga. Further study is needed to conclusively identify the phases with which Ga is associated. This initial work, however, demonstrates success in using XAS in creating a reference library for Ga minerals and identifying unknown Ga minerals in complex mixtures.

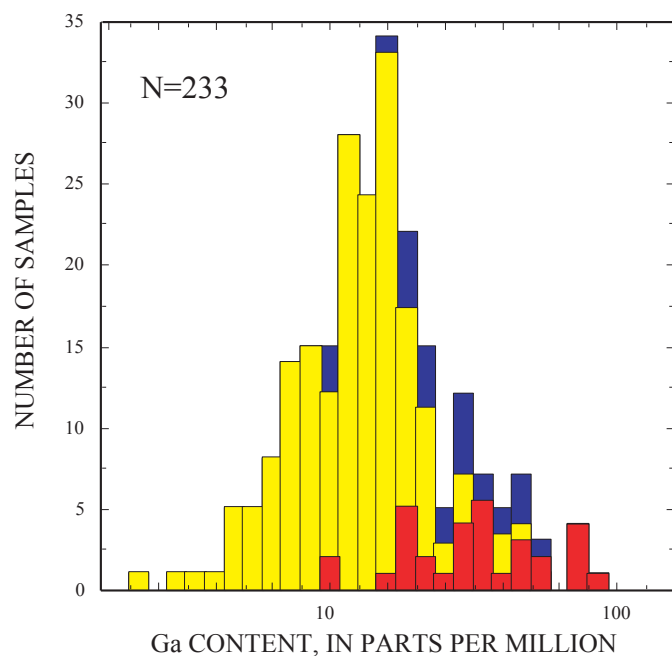


Figure 6. Histogram of Ga contents in 233 drill-hole samples from the McDermitt Hg deposit, Nev. (fig. 4), and adjacent alteration zones. Blue samples are from entire data set, and yellow to red samples represent increasing degree of kaolinite-alunite alteration.

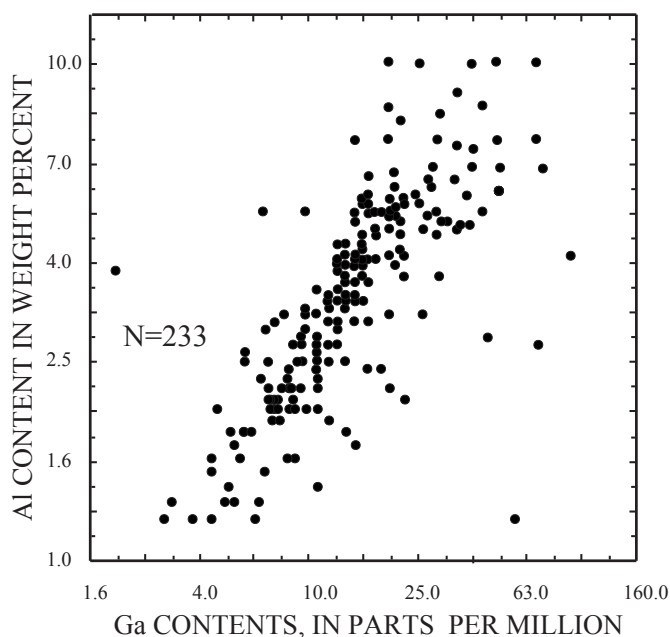


Figure 7. Logarithmic plot of Ga versus Al contents in drill-hole samples from the McDermitt Hg deposit, Nev. (fig. 4), and adjacent alteration zones, showing a correlation of Al with Ga for samples containing less than 30 ppm Ga.

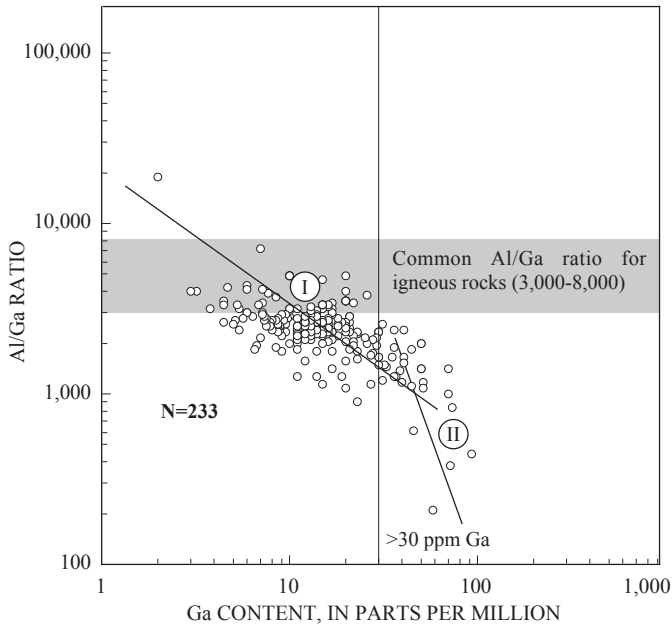


Figure 8. Al/Ga ratio versus Ga content in 223 drill-hole samples from the McDermitt Hg deposit, Nev. (fig. 4), and adjacent alteration zones, separated into samples containing less than 30 ppm Ga with a similar Al/Ga ratio (population I), and samples enriched in Ga (>30 ppm) with a different Al/Ga ratio (population II).

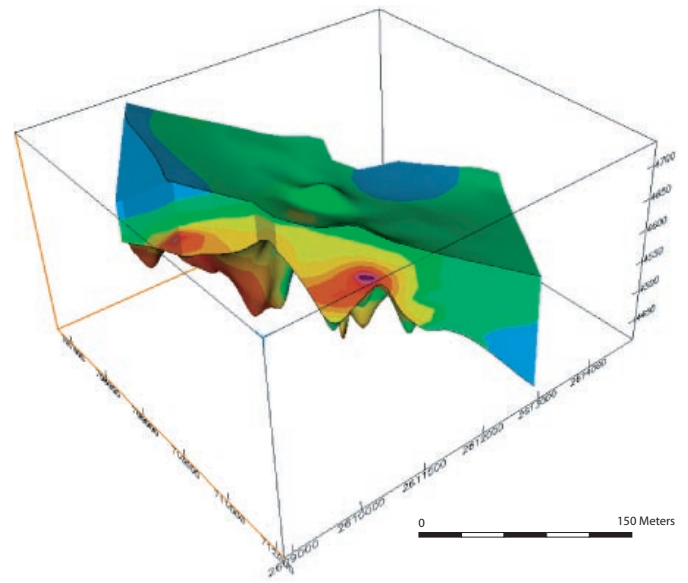


Figure 9. Block diagram showing three-dimensional distribution of Ga in the McDermitt Hg deposit for boxed area in figure 5. Vertical exaggeration, 10 \times ; azimuth, 048.9, inclination, 33.7. Ga content (in parts per million) is colored from low (blue) to high (red), with yellow indicating zone containing 30 ppm Ga.

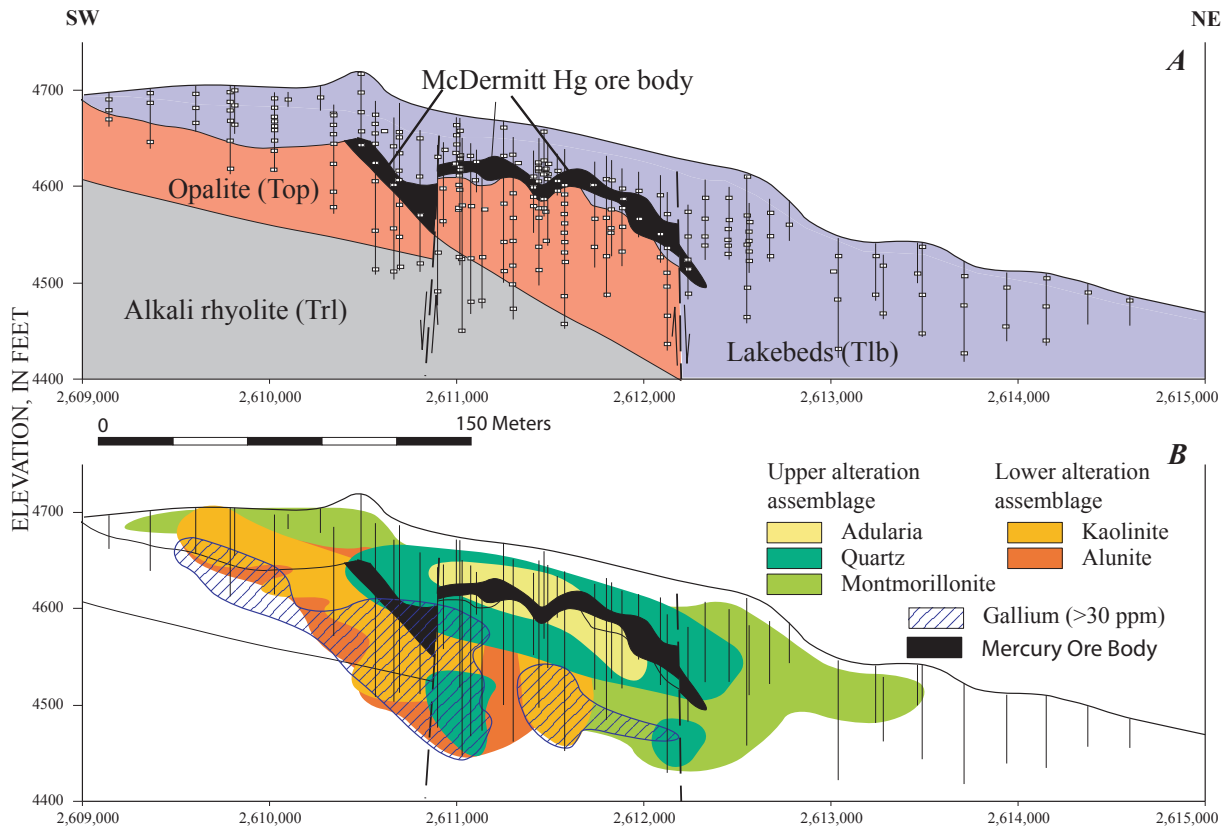


Figure 10. Schematic geologic cross section of the McDermitt Hg deposit, Nev., along southeast wall of block diagram in figure 9, showing distribution of Ga-enrichment zone (A) and alteration assemblages (B). Vertical exaggeration, 4 \times .

Table 4. Major factors of alteration minerals in 233 core samples from the McDermitt Hg deposit, Nev.

[Numbers in bold are significant correlation factors]

Alteration mineral	Factor 1	Factor 2	Factor 3
Adularia -----	-0.121	0.749	-0.092
Albite -----	-.003	.021	-.026
Alunite -----	-.062	-.139	.742
Calcite -----	-.051	.003	.011
Clinoptilolite -----	.777	-.111	.00009524
Cristobalite -----	-.350	-.730	-.111
Kaolinite -----	-.052	-.061	.726
Montmorillonite -----	-.324	-.188	-.735
Mordenite -----	.890	.075	.057
Quartz -----	-.153	.748	-.057

Table 5. General and X-ray-absorption-spectroscopic properties of model compounds and Ga-enriched samples from the McDermitt Hg deposit, Nev., and adjacent alteration zones.

[XANES, X-ray-absorption near-edge structure. ΔE_0 , energy shift (in electron volts); *R*, residual (in percent)]

Model compound	Ga content (ppm)	Local coordination	XANES edge position (± 0.0005 KeV)	Results of least-squares fit using $\text{Ga}_2(\text{SO}_4)_3$	Radial distance from Ga to nearest-neighbor atoms (Å)
GaAs	--	Arsenic nearest neighbors; tetrahedral Ga.	10.3681	--	~2.5
Ga_2O_3	--	Oxygen nearest neighbors; tetrahedral and octahedral Ga.	10.3729	--	~1.3 and ~1.9
$\text{Ga}_2(\text{SO}_4)_3$	--	Oxygen nearest neighbors; octahedral Ga.	10.3750	--	~2.0
AM68-170	58	---	10.3748	$\Delta E_0 = -0.67$, $R = 8.8$	~1.4 and ~1.9
AM34-130	73	---	10.3750	$\Delta E_0 = -0.40$, $R = 8.8$	~1.4 and ~2.0
AM406-145	93	---	10.3751	$\Delta E_0 = -0.32$, $R = 7.6$	~2.0
AM406-190	52	---	10.3757	$\Delta E_0 = 0.22$, $R = 10.1$	--

Conclusions

The Ga enrichment in zones of advanced argillic alteration indicates that hydrothermal processes can concentrate Ga to levels that may be of economic significance. Ga contents in quartz-alunite (high sulfidation) Au and silica deposits indicate that Ga may be enriched in the alunite±kaolinite assemblage adjacent to the vuggy-silica zones that are Ga depleted. The peripheral zones of argillic and propylitic alteration have low Ga contents and have Al/Ga ratios typical of the unaltered volcanic host rocks in this deposit type. Hot-spring-type Hg and Au deposits associated with zones of advanced argillic alteration that formed in near-surface steam-heated environments have low Ga contents. Ga is not concentrated in the acid-condensate fluids that form in these low-temperature deposits, and is depleted in zones of residual silica in acid-leached host rocks. Thus, the geochemical behavior of Ga provides another basis for characterizing the difference in

origin of these two distinct types of alunite-bearing advanced-argillic-alteration assemblages.

The Ga enrichment at the McDermitt Hg deposit has several characteristics that differentiate it from other zones of advanced argillic alteration and hot-spring-type Hg deposits. Both the unaltered and altered volcanic and sedimentary rocks at the McDermitt Hg deposit have a lower Al/Ga ratio and a wider variation in Ga content than those defined by the field for worldwide unaltered volcanic rocks, and than both unaltered and argillically altered rocks at the Paradise Peak Au-Ag-Hg deposit (fig. 3). This difference, in part, likely reflects the lower Al content of the peralkaline volcanic rocks and some of the caldera-fill sedimentary rocks that contain dioctahedral smectite clays with relatively low Al contents. The Ga-enriched, alunite-bearing advanced-argillic-alteration assemblages at the Paradise Peak Au-Ag-Hg deposit generally plot within the field of McDermitt rocks (fig. 3), indicating that high Ga contents are associated with alunite in both of

these deposits. The sample with the highest Ga content from the Paradise Peak Au-Ag-Hg deposit has an Al content indicative of nearly pure alunite (fig. 3). XAS analysis indicates that the Ga-enriched samples from the McDermitt Hg deposit have XANES and EXAFS spectra similar to that of gallium sulfate but that another Ga phase is also present in one of the samples analyzed.

The zone of advanced argillic alteration in most hot-spring-type Hg deposits occurs above the Hg ore body. In a steam-heated environment, Ga is not transported and concentrated but is leached along with other elements by the acid-condensate fluid formed at the ground-water table. Thus, such acid-leached rocks as those at the Paradise Peak Au-Ag-Hg deposit that formed in such an environment have relatively low Ga contents and Al/Ga ratios (fig. 3). At the McDermitt Hg deposit, the zone of advanced argillic alteration is below the Hg ore body, suggesting that the alteration occurred in a magmatic-hydrothermal environment from magmatic SO₂

released from a shallow intrusion. In this environment, Ga is transported and concentrated with alunite and kaolinite. Thus, the zone of advanced argillic alteration at the McDermitt Hg deposit is similar to that associated with quartz-alunite (high sulfidation) Au-silica deposits and may have formed early in the evolution of the hydrothermal system that subsequently formed the hot-spring-type Hg deposit. The highest Ga content in nearly pure alunite from the Paradise Peak Au-Ag deposit indicates that Ga contents in a magmatic-hydrothermal environment reflect a maximum enrichment factor of about 6 compared to Ga relative to the Ga contents in unaltered volcanic rocks. This factor is much less than that observed for most other elements of economic interest that occur in hydrothermal ore deposits. Thus, although Ga enrichment in zones of advanced argillic alteration in magmatic-hydrothermal environments is likely to be common, maximum Ga contents are likely to be only several hundred part per million.

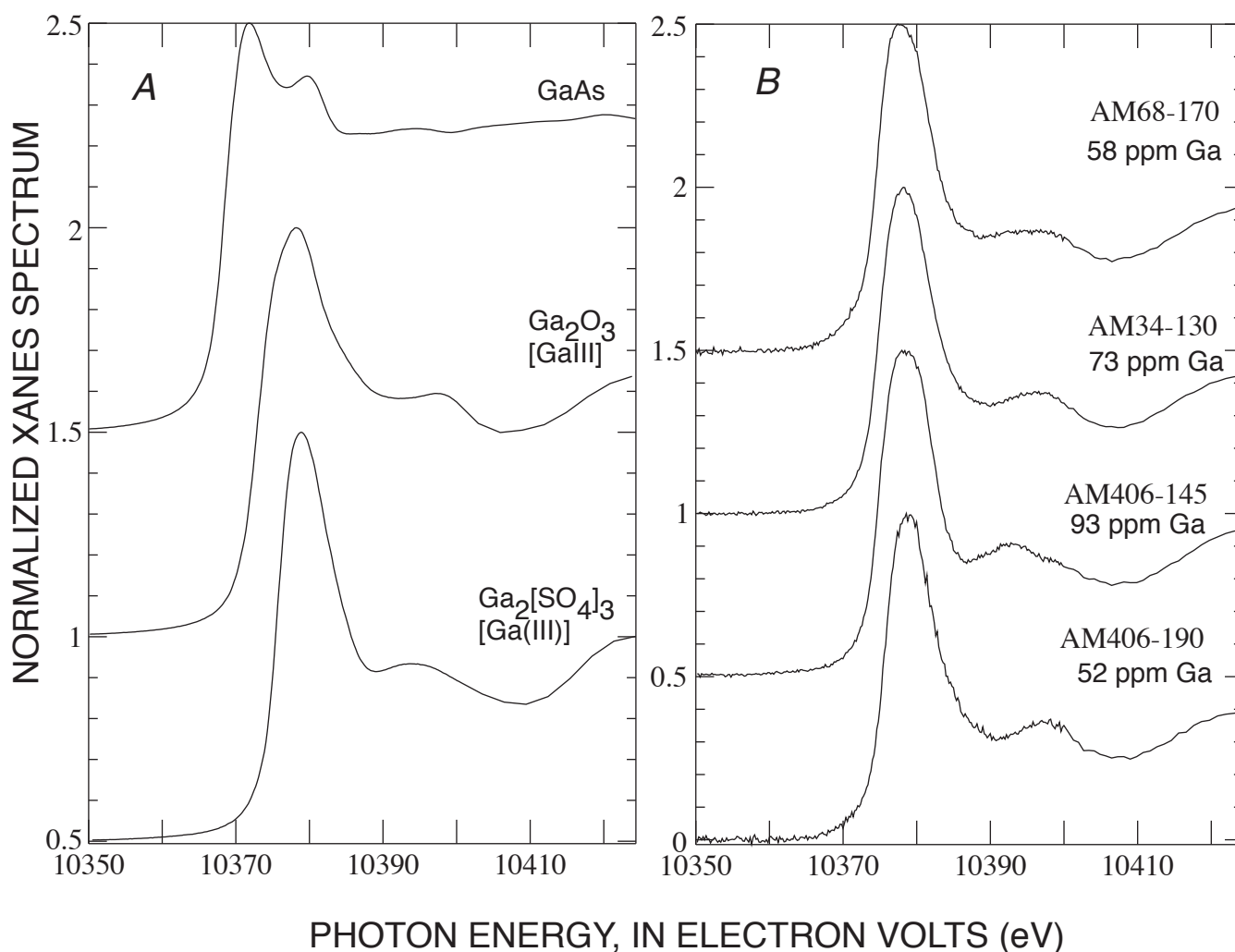


Figure 11. X-ray-absorption near-edge structure (XANES) spectra for reference Ga minerals (A) and for Ga-enriched samples from zone of advanced argillic alteration in the McDermitt Hg deposit (B). Units on vertical scale are arbitrary.

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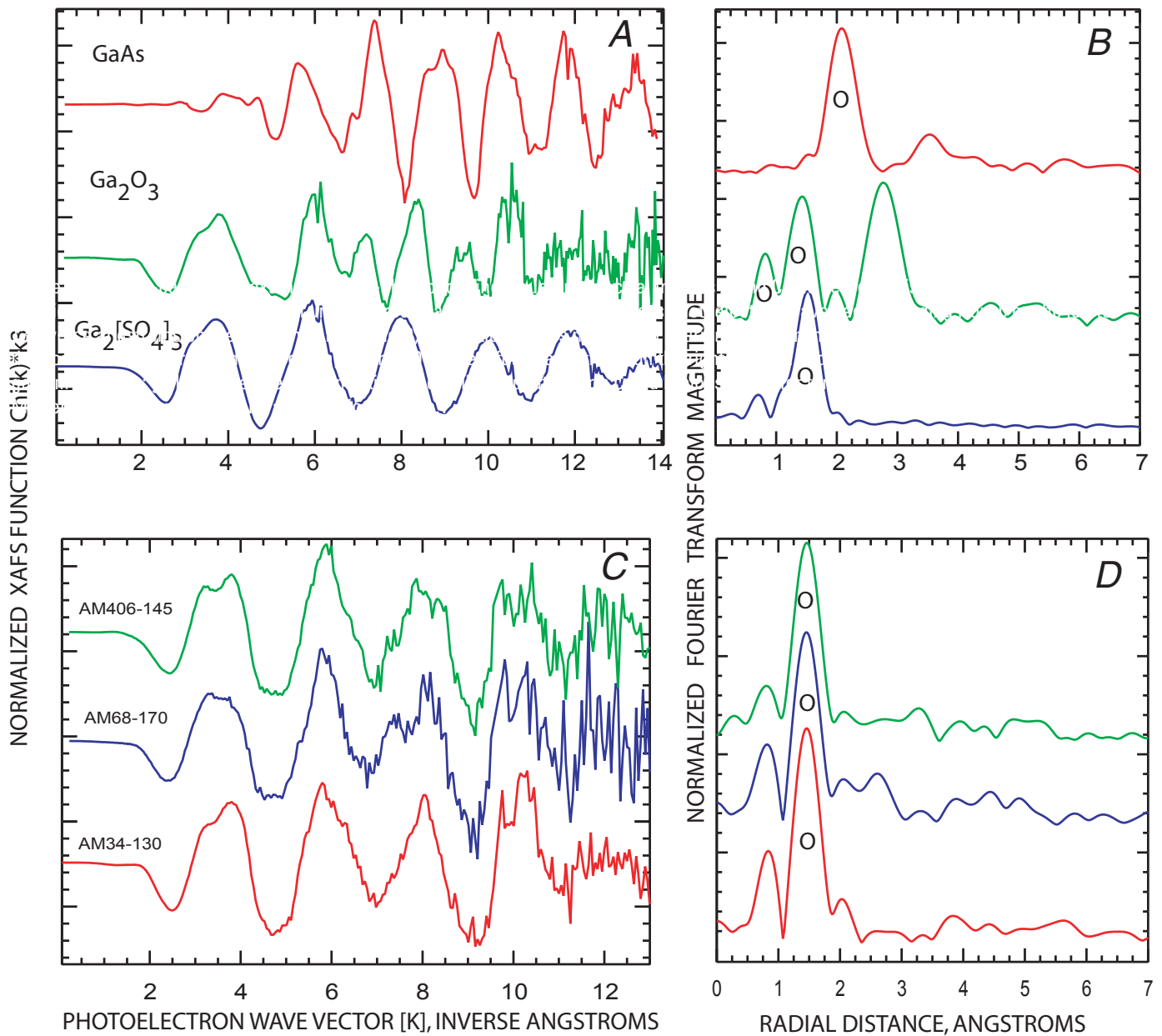


Figure 12. Extended-X-ray-absorption fine-structure (EXAFS) spectra for reference Ga minerals (A, B) and for Ga-enriched samples from zone of advanced argillic alteration in the McDermitt Hg deposit, Nev. (C, D). Units on vertical scale are arbitrary.

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