Annual Report of the Director
Geophysical Laboratory

2801 UPTON STREET, NORTHWEST, WASHINGTON, D.C. 20008

1981–1982

Reprinted from
Carnegie Institution of Washington Year Book 81
for the year July 1, 1981–June 30, 1982
Issued December 1982
Papers from the Geophysical Laboratory
Carnegie Institution
No. 1880
amphibole-rich retrograde alteration that contains the ore minerals. In several tin skarns fluorite-white mica veins carry appreciable quantities of beryl-
lium minerals, very similar to the mus-

covite-fluorite stage at McCullough Butte (e.g., Lost River, Alaska, see Dob-
sont, 1982; Moina, Tasmania, see Kwak

The mineral assemblages, zoning, and
geochemical data (Barton et al., this Re-
port; M. D. Barton, in preparation) in-
dicate low to
{\text{S}_2'}{\text{C}_01}, total Fe, Cu, and Pb
and significant contents of acid, F-
bearing species and the lithophile ele-
ments. These data are consistent with
a low-pressure, moderate-temperature
origin for the alteration resulting from
reaction of the carbonates with fluo-

dine-rich fluids derived from a local
granitic intrusive.

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TRACER STUDIES OF THE FLUORINE-
RICH SKARN AT MCCULLOUGH BUTTE,
EUREKA COUNTY, NEVADA*

M. D. Barton, J. Ruiz,‡ E. Ito,§ and L. Jones§

A central problem in understanding the
 genesis of hydrothermal mineral
 deposits and some other metasomatic
 rocks is the origin of the fluids and non-
 volatile components that form the de-
 posits. Isotope and trace-element studies
can place constraints on these origins

*Research supported in part by an American
Selco grant.
†University of Michigan, Ann Arbor, Michi-
gan.
‡Department of Terrestrial Magnetism.
§CONOCO, Ponca City, Oklahoma.

and other parameters such as temperta-
ures, activities of species in aqueous
solution, and fluid-rock ratios. The is-
topes of H, C, O, and S have been widely
applied to the study of ore deposits (e.g.,
reviews by Taylor, 1979; Ohmoto and
Rye, 1979) and to a lesser extent in the
study of other problems in water-rock
interaction (e.g., Taylor, 1977; Rumble
et al., 1982). Strontium isotope measure-
ments have recently been used to
provide insight into transport and mix-
ing mechanisms in igneous rocks
(James, 1981) and hydrothermal trans-
port in oceanic crust (McCullough
et al., 1981), a granite (Dickin
et al., 1980), and a fluorite deposit (Ruiz et al., 1980).
James (1981) reviewed the use of com-
bined oxygen and strontium isotope
studies in resolving the sources of com-
ponents in igneous systems. The rare
earth elements (REE) are most com-
monly used to decipher the evolution of
igneous rocks (reviewed by Hanson,
1980), but recently Exley (1980) and
Daigneault et al. (1982) used the REE
in studies of fluid-rock interactions.

In this study C, O, and Sr isotopes
and the REE are used to evaluate the
sources of components and to estimate
fluid-rock ratios for the fluorine-rich
skarn at McCullough Butte, Eureka
County, Nevada. These results, in com-
bined with those from ongoing geo-
ological and geochemical studies of the
McCullough Butte skarn (Barton, this
Report), will provide a detailed descrip-
tion of the alteration that should bear on the mechanisms of for-
mation of other skarns and fluorine-rich
mineral deposits.

Carbon and Oxygen Results

The isotopes of carbon and oxygen are
useful tracers of the ore-forming com-
ponents at McCullough Butte because the
different possible sources of the
components of the alteration (marine
carbonate, granite porphyry, and me-
teoric water) have significantly differ-
ent initial isotopic ratios. The
combination, during the alteration process, of equilibrium isotopic fractionation among phases and mass transfer should produce isotopic variations that reflect the sources of components.

A total of 45 samples of calcite and dolomite, representing each of the alteration types at McCullough Butte (see Barton, this Report) and the host carbonates, were analyzed for their C and O isotope ratios with standard techniques. The results of these analyses are plotted in Fig. 37 with both C and O referred to the PDB scale. For comparison, the ranges of magmatic and meteoric oxygen, magmatic carbon, and Ordovician limestone are shown.

The isotopic results separate groups of carbonates in the area. Fresh limestones and dolomites far from the fluorine-rich alteration have values like those for unaltered carbonates of similar age elsewhere. Compared with the fresh carbonate rocks, the vein-filling carbonates from the Ag veins are depleted in $^{18}O$ but little changed in $^{13}C/^{12}C$. In contrast, the fluorine-rich alteration and its host carbonates show marked depletion in both $^{13}C$ and $^{18}O$ along a trend toward magmatic values. Generally, in the fluorite-bearing vein associations the vein carbonates are the most depleted, the skarn carbonates are less so, and the host carbonates are the least depleted. The lightest value belongs to a coarse calcite crystal from a pegmatitic vein cutting the granite porphyry.

The depletion in $^{18}O$ and not in $^{13}C$ for the Ag veins is consistent with a fluid dominated by meteoric water and a high, cumulative fluid/rock value. In the skarn, the depletion in both $^{18}O$ and $^{13}C$ is compatible with a dominantly magmatic fluid. Decarbonation reactions, which produce similar patterns, could have played a significant role. Large-scale interaction with pristine meteoric water is unlikely for the skarn because the $^{18}O$ is insufficiently depleted. Fluid-rock ratios, however, are difficult to estimate because they depend on model assumptions and detailed knowledge of the physical

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**Fig. 37.** Plot of $\delta^{13}C$(PDB) vs. $\delta^{18}O$(PDB) showing the isotopic compositions of 45 carbonate samples from the McCullough Butte area. The range for meteoric water is from Taylor (1979), the magmatic carbon range is from Ohmoto and Rye (1979), and the magmatic water range is estimated from preliminary isotopic analyses of the igneous silicates.
conditions during petrogenesis. The magmatic source of oxygen and carbon for the skarn is similar to that found by Taylor and O’Neil (1977) for skarns in the Osgood Mountains.

**Strontium and REE Results**

Strontium and the REE usually substitute for calcium in minerals, albeit to different degrees. Because calcium phases are abundant in the McCullough Butte rocks and because the different rock types should have different initial REE patterns and Sr isotope ratios, these elements can yield evidence about sources of components. The strontium isotopes have the added advantage that they do not fractionate in geological processes; therefore, they can be used as absolute tracers independent of the physical conditions of ore formation (providing that corrections for radiogenic Sr are made). Neodymium isotope measurements could potentially be used in the same way as Sr ratios to determine the sources of the REE.

Strontium isotope analyses for fifteen samples are presented in Fig. 38; they were performed with standard techniques at the CONOCO laboratories, Ponca City, Oklahoma, and at the Carnegie Institution Department of Terrestrial Magnetism. Corrections for radiogenic strontium were made to several of the granite (Kg) ratios. Ten REE analyses were done by instrumental neutron activation analysis at the University of Michigan. The REE patterns show strong light REE enrichments (relative to chondrites) in the granite porphyries, and flatter, less fractionated patterns in the host carbonates. Fluorite REE patterns resemble those of the host rocks.

The intermediate strontium ratios for the fluorite (Fig. 38) require mixing of Sr from at least two sources. Multiple-source origin contrasts with the results of Ruiz et al. (1980) on the fluorite deposit at Las Cuevas, where all the Sr was locally derived. The REE results suggest a more limited mobility for those elements, in agreement with experimental partition coefficients (Flynn and Burnham, 1978) but somewhat different from recent studies on other hydrothermal systems (Exley, 1980; Daigneault et al., 1982).

**Conclusions**

The C, O, and Sr isotopic results indicate that magmatic fluids played a large part in the formation of the McCullough Butte skarn. The patterns suggest that the REE were relatively immobile, even under the F-rich (and possibly CO$_2$-rich) conditions of formation.

**References**


STABILITY OF SPODUMENE IN ACIDIC AND SALINE FLUORINE-RICH ENVIRONMENTS

David London

The subsolidus alteration of spodumene to mica-bearing assemblages is significant for two reasons: (1) replacements of this type are commonly observed in spodumene-bearing pegmatites, and thus the processes involved are of general significance to pegmatite evolution, and (2) economic deposits of tantalum are usually associated with mica-bearing assemblages that have replaced spodumene. Preliminary experimental studies of the effects of aqueous $H^+$, $K^+$, and $F^-$ on the stability of spodumene include those of Armstrong (1969), Munoz (1971), and Grubb (1973). Natural occurrences of altered spodumene and associated phases (Table 14 and Fig. 39) provide qualitative information that can be organized in schematic isobaric, isothermal $\mu$HF-$\mu$KF-$\mu$LiF acidity-salinity phase diagrams (e.g., Burt, 1981). The phase diagrams depicted in Fig. 40 present sequences of mineral reactions involving spodumene and other phases in the system LiAlO$_2$-SiO$_2$-H$_2$O-HF-LiF-KF. The sequences of assemblages produced by increasing fluid acidity ($\mu$HF) reflect the increasing capacity of an aqueous fluid to hydrolyze solid phases and leach alkali cations. Increasing salinity ($\mu$KF) also reflects increasing alkalinity of the fluid phase, because some of the reactions listed in Table 15 and shown in Fig. 40 are actually exchange reactions. For example, the conversion of spodumene to K-feldspar with increasing $\mu$KF could be represented by the component KLi$_2$-$J$, an alkaline exchange operator, which is equivalent to

$$\mu_{\text{K}} - \mu_{\text{L}} + RT \ln(a_{\text{K}}/a_{\text{L}}).$$

Figure 40 is constructed for an arbitrary $P$ and $T$ within the stability field of spodumene (e.g., 300°–400°C and 2–

<table>
<thead>
<tr>
<th>Phase</th>
<th>Abbreviation</th>
<th>Composition</th>
</tr>
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<tbody>
<tr>
<td>Topaz</td>
<td>Tpz</td>
<td>Al$_2$SiO$_4$F$_2$</td>
</tr>
<tr>
<td>Cookeite</td>
<td>Ckt</td>
<td>Li$_2$SiO$_4$(OH)$_6$</td>
</tr>
<tr>
<td>Muscovite</td>
<td>Mus</td>
<td>KAl$_2$Si$_2$O$_5$(OH)$_4$</td>
</tr>
<tr>
<td>Lepidolite</td>
<td>Lpt</td>
<td>K$_2$Li$_2$Al$_2$Si$_2$O$_8$(OH)</td>
</tr>
<tr>
<td>Spodumene</td>
<td>Spd</td>
<td>LiAlSi$_2$O$_6$</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>Ksp</td>
<td>KAlSi$_2$O$_8$</td>
</tr>
<tr>
<td>Quartz</td>
<td>Qtz</td>
<td>SiO$_2$</td>
</tr>
</tbody>
</table>

TABLE 14. Names and Compositions of Phases under Consideration