

Arc-related sodic hydrothermal alteration in the western United States

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ABSTRACT

Sodium-rich hydrothermal alteration is widely developed in Permian to Jurassic arc igneous rocks of the western United States, but it is rare in younger rocks. Na-rich alteration reflects both paleogeographic and igneous compositional controls. Two varieties of alteration, NaCa and Na, can be defined by mineralogic and compositional changes. Both are common in Permian to Jurassic arc plutonic and volcanic rocks and are accompanied by Fe and Cu \pm Zn mineralization. Geologic relationships and mineralogic, stable isotopic, and fluid-inclusion data indicate that the fluids responsible for sodium-rich alteration were isotopically heavy, moderately to highly saline fluids of marine, formation, and/or meteoric origin, with or without a magmatic component. The transition away from widespread Na \pm Ca-rich alteration in the late Mesozoic corresponds to and is consistent with the change from an early Mesozoic marine and/or arid rifted-arc setting to a fully emergent, continental arc environment in the Cretaceous.

INTRODUCTION

Hydrothermal alteration accompanying magmatism is profoundly influenced by the geologic environment. Hydrothermal alteration is universally acknowledged as a major process at spreading centers, where interaction of seawater and the oceanic crust leads to extensive sodium-rich alteration (e.g., Seyfried et al., 1988). Analogous circulation of surface waters in terrestrial environments typically has more subtle, though commonly widespread results (e.g., Criss and Taylor, 1986). Metasomatic effects in marine and rifted arc environments, which have characteristics of both, however, are less well known (see Barton et al., 1991a). Where described, marine arc rocks are typically altered to a variety of greenschist and zeolite facies hydrothermal assemblages that commonly show evidence of mass transfer; these are commonly characterized as spilites or keratophyres.

In this paper, we summarize our studies and those of others that describe Na-rich alteration associated with Mesozoic arc igneous rocks of the western United States. This alteration is similar to but differs in several aspects from better known seafloor alteration. We suggest that Na-rich alteration is a common feature in pre-Cretaceous arc-related igneous rocks of the western United States and that it reflects a spectrum of tectonically related geologic environments.

DESCRIPTION OF ALTERATION

Sodium-rich alteration developed in western United States arc igneous rocks is of two basic types, distinguished by mineral assemblages and bulk chemical compositional changes: sodic-calcic ("NaCa") and sodic ("Na"), following the nomenclature of Carten (1986). Both types result in the replacement of igneous feldspars by more Na-rich framework silicates and the development of distinctive ferromagnesian minerals. NaCa and Na alteration are regionally and volumetrically important, occurring in many mafic to felsic igneous rocks from southern Arizona through northern Oregon (Fig. 1 and Table A¹). A third type, sodic-potassic ("NaK") alteration is uncommon, volumetrically minor, and, unlike Na ± Ca alteration, largely compositionally restricted to Late Cretaceous age two-mica granites. NaK alteration is distinct from early Mesozoic style Na ± Ca alteration (Barton,

1987) and will not be addressed here. The different types of alteration are distinguished in this paper to the extent that available descriptions allow.

Alteration Mineralogy and Composition

Both types of sodium-rich alteration produce distinctive mineral associations (Table 1) that reflect contrasting metasomatic changes. Whole-rock analyses of NaCa and Na altered arc rocks from several locations are available in published literature (e.g., Hanson et al., 1993; Muffler, 1964; Carten, 1986); discussion of new X-ray fluorescence analyses of fresh and altered equivalent rocks is also included here. All major element analyses were normalized for comparison to anhydrous fresh whole-rock equivalents assuming Al conservation. This restriction is unrealistic in detail; however, general patterns are coherent, and rock textures indicate that large volume changes did not occur as would be expected if Al were highly mobile. Mineral assemblages similar to those described here can be produced by other mechanisms such as retrograde hydration and low-pressure metamorphism of plagioclase and mafic-mineral-bearing rocks. Consequently, identifying alteration types requires evidence for bulk compositional change.

Rocks affected by NaCa alteration are characterized by large increases in Na and Ca, depletion of K and commonly Fe, and variable changes in Mg. These changes typically occur during development of an albite-oligoclase + actinolite association. Sodic feldspar after K-feldspar is commonly chessboard patterned, indicating its replacement origin (e.g., Gilluly, 1933). Diopside accompanies or replaces actinolite as the dominant ferromagnesian alteration mineral at a few locations (Buffalo Mountain, Shamrock). Scapolite is a common minor constituent in some areas; marialitic scapolite is dominant in parts of the mafic Humboldt complex (Table 1).

In contrast, Na alteration results in the addition of Na, leaching of Ca and K, and variable changes in Fe, Mg, and Mn, which is reflected in the characteristic albite + chlorite association with variable mineral proportions. As with NaCa alteration, secondary

plagioclase can be chessboard patterned, and marialitic scapolite is a common associate. Analcime is a widespread component of Na alteration in the Humboldt complex.

The identities and/or compositions of accessory minerals associated with Na-rich alteration are distinctive. Secondary sphene and rutile are widespread in many Na \pm Ca altered rocks. In contrast, in igneous assemblages, Ti usually occurs in Fe oxides and dispersed in ferromagnesian silicates; sphene is common only in relatively calcic rocks. Accessory hydrothermal scapolite and apatite are both Cl-rich. Scapolite at Humboldt is among the most Cl-rich documented (Vanko and Bishop, 1982), and similar compositions have been inferred elsewhere (Shamrock, Buffalo Mountain).

Alteration Patterns

The early Mesozoic-late Paleozoic hydrothermal systems containing Na \pm Ca alteration exhibit distinctive temporal and spatial alteration patterns. Alteration is typically regional in extent and is extensively developed in both plutonic and coeval volcanic rocks. Where both types are present, Na alteration is shallower and overprints NaCa alteration (Yerington, Humboldt, Cortez). Both varieties are fracture-controlled; alteration envelopes around veins commonly overlap, creating large volumes of pervasively altered rock. Brecciation is well developed in some areas where it is intimately associated with hydrothermal activity (Buffalo Mountain, Yerington, Humboldt, Cortez, Sparta). Dikes cut and are cut by alteration, demonstrating that magmatism persisted during hydrothermal activity (Dilles and Einaudi, 1992; Johnson et al., 1993).

Areas affected by Na \pm Ca alteration routinely contain other alteration types. Hydrolytic alteration, including intermediate argillic, sericitic (in felsic rocks), and chloritic (in mafic rocks) types, is widely developed in many occurrences, where it is shallow and/or late compared to Na \pm Ca alteration. Potassic alteration is well developed at Cortez, the Ritter Range, the White Mountains, and at Yerington, where it and overlying sericitic alteration are both above and central to NaCa and Na alteration (Carten, 1986; Dilles and Einaudi, 1992). Analogous relations have been inferred in other areas, including Humboldt and Cortez

(Johnson et al., 1993). Mineralization associated with these systems includes Fe and Cu deposits of several types, including Fe skarns (e.g., Iron Hat), Fe-oxide replacement bodies (e.g., Cortez), Cu porphyry and skarn mineralization (e.g., Yerington), and volcanogenic massive sulfide deposits (Sierra Nevada foothills). Mass balance studies at Yerington indicate that leaching of the granitoids may have provided up to 30% of the Cu in the Ann Mason porphyry Cu deposit (Dilles and Einaudi, 1992). Rocks associated with Fe-P deposits in the Humboldt and Cortez Mountains areas show that bulk compositional changes during high-temperature alteration can account for the Fe, P, and rare earth element contents of the associated mineral deposits (Barton et al., 1991b).

Spatial and Temporal Distribution

Na-rich alteration is present throughout the late Paleozoic to Jurassic igneous rocks of the western United States. Voluminous Na ± Ca alteration is virtually absent in Cretaceous and younger rocks, one exception being the Paleocene Ajo district (Gilluly, 1946). With few exceptions, Na ± Ca alteration occurs in igneous rocks near or west of the former Paleozoic continental margin (Fig. 1). Na alteration is widely developed in arc plutonic and volcanic rocks; in some areas (e.g., Sierra Nevada foothills, Seven Devils region, Klamaths), it is regionally extensive in volcanic and hypabyssal rocks, affecting tens to hundreds of square kilometres. These areas most closely resemble spilitized arc terranes. Elsewhere, as in most of the Great Basin occurrences, Na alteration tends to be more spatially restricted. In these areas, hydrolytic alteration appears to be more common along with Fe-oxide or Cu mineralization. NaCa alteration is less well documented in published literature, but is apparently also common, particularly in the inboard (more eastern) occurrences (Table A). Volumes may reach tens of cubic kilometres (e.g., Humboldt, Yerington).

Na ± Ca alteration in the western United States is dominantly a shallow process; altered intrusions are epizonal, and alteration typically affects comagmatic volcanic rocks. Depths of alteration are well constrained at Yerington, where NaCa and Na alteration affect rocks from paleodepths of 3.3 to >6 km and 1 to 4 km, respectively (Dilles and Einaudi, 1992).

This depth range is supported elsewhere by the common abundance of volcanic rocks and intrusive textures consistent with hypabyssal environments. Mineralogic and isotopic constraints on temperatures are also consistent with epizonal settings; NaCa alteration occurs at moderate temperatures (~300-500 °C), whereas lower temperatures (~200-400 °C) are typical of Na alteration (Dilles and Einaudi, 1992; Carten, 1986; Vanko and Bishop, 1982).

STABLE ISOTOPE GEOCHEMISTRY

Both varieties of Na-rich alteration are accompanied by appreciable shifts in isotopic composition (Dilles et al., 1992; Fox, 1989; Hall et al., 1988; Hanson et al., 1993; this study). NaCa altered rocks yield $\delta^{18}\text{O}$ of 6.0‰ to 11.6‰ on hydrothermal plagioclase and quartz, and δD of -67‰ to -116‰ on hydrous mafic minerals. Secondary plagioclase in Na-altered rocks generally has $\delta^{18}\text{O}$ in the range 4.9‰ to 14.1‰, although lower values have been documented in central and southern California (Hall et al., 1988; Fox, 1989). Measured chlorites from Na-altered rocks have δD of -78‰ to -92‰. As with $\delta^{18}\text{O}$, lighter δD values appear restricted to southern occurrences. These results are consistent with heavy to intermediate isotopic values ($\delta^{18}\text{O} = 2‰$ to $8‰$, $\delta\text{D} = -35‰$ to $-90‰$) for aqueous fluids related to Na \pm Ca alteration. Limited $\delta^{34}\text{S}$ determinations of sulfides in Jurassic Fe-oxide-rich systems in Nevada give values ranging from +6‰ to +16‰ (Barton et al., 1991b). These compositions contrast with lighter sulfide $\delta^{34}\text{S}$ values found in other hydrothermal systems, while approaching the $\sim+18‰$ composition of Jurassic marine sulfate (Claypool et al., 1980).

FLUID SALINITIES

Fluid inclusion and phase equilibria indicate that Na \pm Ca fluids were relatively saline. Fluid inclusions in NaCa altered rocks from Yerington indicate salinities of 31 to 41 wt% equivalent NaCl; later sodic fluids were likely of more moderate salinity (Dilles and Einaudi, 1992). Fluid inclusions in prograde assemblages at Iron Hat imply that highly saline fluids

were responsible for albitization (Hall et al., 1988). Experimental work on scapolite stability indicates that highly saline fluids (>40 mol% NaCl) are required to produce marialitic scapolite as in the Humboldt complex (Vanko and Bishop, 1982), an interpretation supported by common high-salinity fluid inclusions in these rocks. The large volumes of Na and NaCa alteration provide a further indication of moderate to high salinities, because it would be difficult to transport sufficient mass with dilute fluids. Most of the evidence for highly saline fluids comes from the NaCa-bearing systems east of the Sierra Nevada; it is possible that salinities were not as high in the systems that contain Na alteration alone. The latter systems, such as those in the Sierra Nevada foothills and Klamath spilitic regions, closely parallel many seafloor hydrothermal systems (Zierenberg et al., 1988).

FLUID SOURCES

Fluids that produced NaCa and Na alteration had intermediate to heavy isotopic compositions and were moderately to highly saline. The fluid isotopic compositions and the volumes of altered rocks likely preclude magmatic water as the sole source of the hydrothermal fluids, although magmatic sources may have been important contributors as at Iron Hat. Formation waters have salinities and O, H, and S isotopic compositions consistent with those inferred for Na ± Ca alteration. In contrast, the isotopic composition and salinity of seawater and meteoric water are distinct from those of calculated equilibrium waters. However, increasing incorporation of seawater and/or isotopically heavy meteoric water (consistent with a low-latitude coastal setting) into a hydrothermal system initially dominated by magmatic fluids could yield the appropriate salinities and isotopic compositions. Alternatively, fluids may have been derived from evaporitic rocks of the early to middle Mesozoic and/or from saline and alkaline surface waters formed in the arid environment and (partially) enclosed basins characteristic of this time (Peterson, 1988; Turner and Fishman, 1991; cf. Fig. 1), as has been suggested at Yerington (Dilles and Einaudi, 1992). This would fit the somewhat lighter values inferred for waters in southern parts of the arc.

ORIGINS AND SIGNIFICANCE OF SODIUM-RICH ALTERATION

Sodium-rich alteration has been widely studied only in marine spreading centers, even though keratophyres and spilites are described worldwide. Sodic alteration is widely noted, for example, in studies of arc-related middle Mesozoic Fe(-Cu) deposits in the central and southern Andes, where geochemical data indicate a seawater-like component (e.g., Ripley and Ohmoto, 1977). Its widespread occurrence in early Mesozoic arc igneous rocks of the western United States suggests that it may be a common feature in some arc settings. The distinctive characteristics of Na ± Ca alteration in the western United States indicate a common mode of formation and suggest an environmental control on alteration. Although the lack of recognition of Na-rich alteration might be due to rarity, it seems more likely that it is a consequence of igneous petrologists focusing on fresh rocks and economic geologists looking primarily at ore deposits, which are typically more closely associated with other alteration types.

On the basis of geochemical and geological data presented above, experimental work on processes that potentially produce Na-rich alteration, and paleogeographic constraints, we propose that Na-rich alteration reflects two types of processes that operate in arc environments: (1) infiltration of Na-enriched fluids, and (2) changes in temperature along a fluid path. In the first case, infiltration of ocean water with its high Na/Ca leads to spilitization at spreading centers and, presumably, in at least some marine arc environments (e.g., Seyfried et al., 1988). Similarly, infiltration of formation waters or evaporitic brines with high Na/K and Na/Ca could produce highly sodic assemblages. In the second case, heating of Cl-rich fluids in equilibrium with alkali feldspars can lead to sodic alteration (Orville, 1963; Carten, 1986). Alternatively, cooling of Cl-dominated fluids with plagioclase can lead to exchange of fluid Na for feldspar Ca (Orville, 1972).

A paleogeographic control on source waters is evidenced by the distribution of Na ± Ca alteration near or west of the early Mesozoic continental margin, where magmas were emplaced in a low-lying arc and marginal basin environment (e.g., Saleeby and Busby,

1992; see Fig. 1). Paleogeographic evidence indicates arid-alkaline surface characteristics for southwestern North America during the early Mesozoic (Peterson, 1988). Western Utah through western Nevada contain distributed marine and lacustrine evaporite deposits of early to mid-Jurassic age (Stewart, 1980; Turner and Fishman, 1991). The paleogeographic environment of southeastern California and southern Arizona during the early Mesozoic is less clear, but the majority of the evidence suggests an extensive, low-lying volcanic pile interfingering with eolian sands (Tosdal et al., 1988), perhaps along a grabenlike arc (Busby-Spera, 1988) that may have accommodated alkaline lakes or restricted marine basins. This alkaline environment during the early Mesozoic could have provided the isotopically heavy, saline fluid(s) necessary for the development of widespread, Na-rich alteration.

Both seawater and isotopically heavy, coastal meteoric water, with or without magmatic fluids, are compatible with the paleogeographic setting and available geochemical data. Seawater is the likely fluid in the western, clearly marine Jurassic ophiolitic rocks (e.g., Klamaths, Sierra Nevada foothills). For most of the sodically altered regions, formation water is the best candidate, perhaps modified through interaction with late Paleozoic and early Mesozoic evaporites. The lack of similar Na-rich alteration in younger igneous rocks of these areas may indicate that the older fluids associated with the evaporites were depleted with time or that alteration resulted from broadly saline surface waters of the arid early Mesozoic environment.

The shift away from voluminous Na \pm Ca alteration at the end of the Jurassic coincides with the transition to an emergent, fully continental arc setting in the Cretaceous. Rare albited Cretaceous rocks lack the distinctive associations of Na \pm Ca alteration and bear no direct relationship to the continental margin. Inasmuch as Na \pm Ca alteration in the western United States is a product of the paleogeographic-tectonic environment, we propose that analogous alteration is a characteristic result of hydrothermal circulation of saline fluids in the shallow portions of rifted and/or extensional back-arc settings.

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TABLE 1. GENERALIZED MINERAL ASSEMBLAGES AND REACTIONS, Na-RICH ALTERATION

| Alteration type | Assemblage | Typical mineral reactions | Rock type |
|-----------------|----------------------|--|-----------------|
| NaCa | 1. sodic plag + act | Intermediate plag, ksp → ab-olig; hbd, biot → act | felsic to mafic |
| | 2. sodic plag + diop | Intermediate plag, ksp → ab-and; hbd, biot → diop | felsic to mafic |
| | 3. scap + act | Intermediate plag → scap; hbd → act ± chl | gabbro, diorite |
| Na | 1. ab ± chl ± qz | Intermediate plag, ksp → ab ± ser; hbd, biot → chl ± act | felsic to mafic |

Note: ab = albite, act = actinolite, and = andesine, biot = biotite, chl = chlorite, diop = diopside, epi = epidote, hbd = hornblende, ksp = K-feldspar, olig = oligoclase, plag = plagioclase, qz = quartz, scap = scapolite.

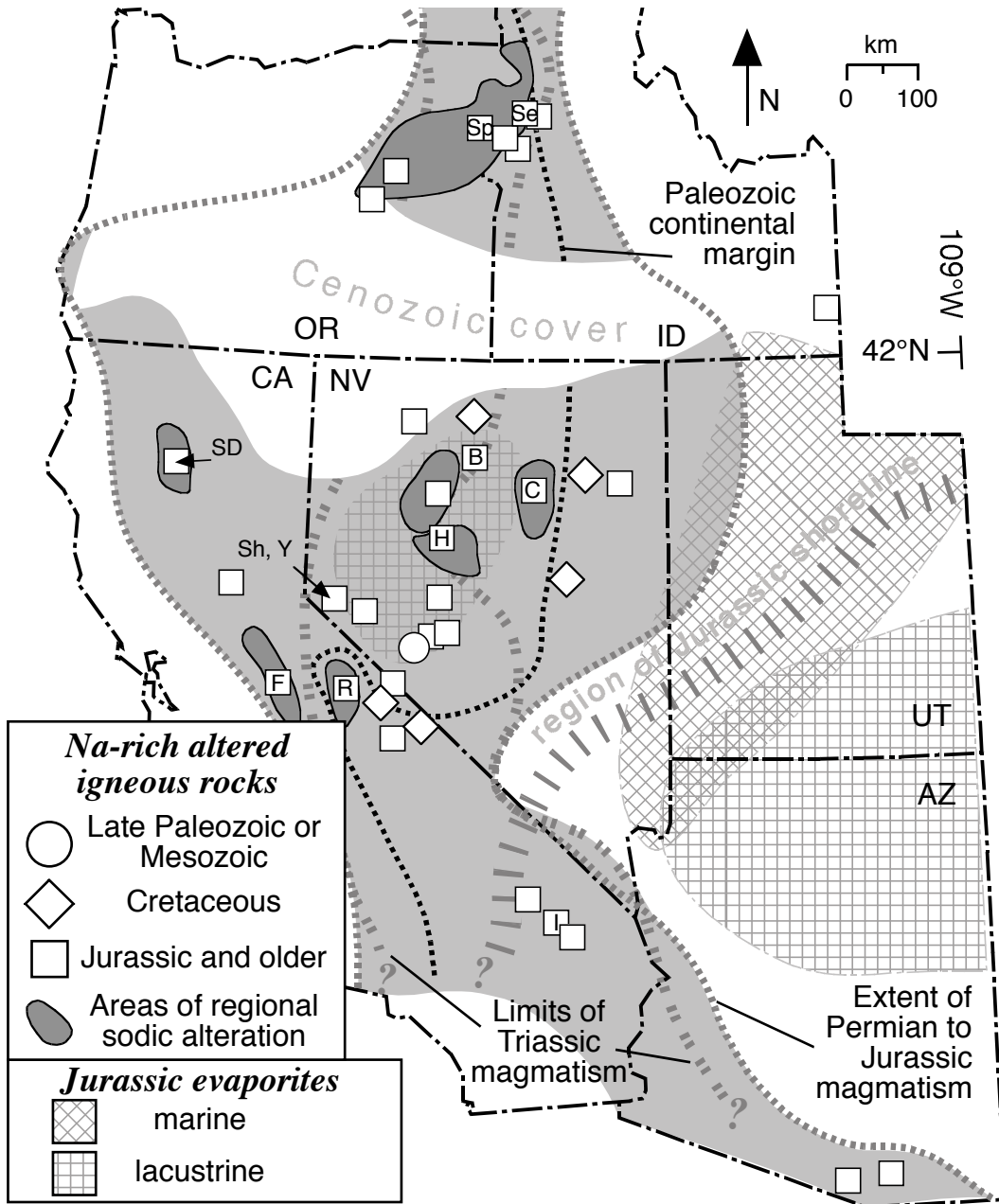


TABLE A. Summary of Na-Rich Alteration, Western United States

| ID # | LOCATION | AGE ¹ | ALTERATION | PRIMARY REFERENCES ² |
|-------------------|--|------------------|--------------|---|
| <i>ARIZONA</i> | | | | |
| 1 | Ko Vaya Super Unit intrusions | J | Na, NaCa? | Tosdal et al., 1989; Riggs, 1987 |
| <i>CALIFORNIA</i> | | | | |
| 2 | Benton Range | Tr | Na, NaCa | Crowder and Ross, 1973; this study |
| 3 | Birch Creek | K | NaK | Barton, 1987; this study |
| 4 | Bristol Mountains | J | Na, NaCa | Fox, 1989 |
| 5 | Iron Hat | J | Na, NaCa | Hall et al., 1988; this study |
| 6 | McGee Mountain | K? | Na | Rinehart and Ross, 1964 |
| 7 | Mule Mountain pluton | Dev | Na | Albers, 1964; Kinkel et al., 1956 |
| 8 | Pellessier Flats | J | Na | Crowder and Ross, 1973; Anderson, 1937 |
| 9 | Pit River stock | PTr | Na | Albers and Robertson, 1961 |
| 10 | Ritter Range | J | Na, "alkali" | Hanson et al., 1993 |
| 11 | Shasta district volcanic rocks | Pal - Tr | Na, NaCa? | Kinkel et al., 1956; Albers and Robertson, 1961; Casey and Taylor, 1982 |
| 12 | Sierra Nevada Foothills | J | Na | Xenophontos and Bond, 1978; Saleeby et al., 1989; Albers, 1981 |
| 13 | Smartville | J | Na | Xenophontos and Bond, 1978 |
| 14 | Soda Mountain Fm. and intrusions | TrJ | Na, NaCa? | Grose, 1959 |
| 15 | Tungsten Hills | Tr | Na | Chen and Moore, 1982; this study |
| <i>IDAHO</i> | | | | |
| 16 | Cuddy Mountain | TrJ | Na | Fankhauser, 1969 |
| 17 | Riggins Group and intrusions | Tr? | Na, NaCa? | Hamilton, 1963 |
| 18 | Seven Devils Group | PTr | Na | Vallier, 1977; Fankhauser, 1969 |
| 19 | Seven Devils intrusions | TrJ | Na, NaCa? | White, 1968 |
| 20 | Unnamed tuff | J | Na | Gulbrandsen and Cressman, 1960 |
| <i>NEVADA</i> | | | | |
| 21 | Buffalo Mtn. pluton | J | NaCa, Na | Neff, 1969; this study |
| 22 | Cortez Mountains | J | Na, NaCa? | Muffler, 1964; this study |
| 23 | Dawley Canyon | K | NaK | Olson and Hinrichs, 1960; Barton, 1987; this study |
| 24 | Gray Hills pluton | J | Na, NaCa? | Bingler, 1978; this study |
| 25 | Happy Creek volcanic series and intrusions | P | Na | Willden, 1963 |
| 26 | Humboldt complex | J | NaCa, Na | Speed, 1963; Vanko and Bishop, 1982; this study |
| 27 | Illinois stock | J | NaCa | Humphrey and Wyatt, 1958 |
| 28 | Koipato volcanic rocks and intrusions | PTr | Na | Tatlock, 1961; Johnson, 1977; Knopf, 1924; this study |
| 29 | McCullough Butte | K | NaK | Barton, 1987 |
| 30 | Melrose pluton | J | NaCa | Stubbs, 1984; Leland, 1990 |
| 31 | Mt. Siegel batholith | J | NaCa, Na | Battles, 1990; this study |
| 32 | Osgood Mtns. intrusions | K | Na, NaK? | Hotz and Willden, 1964; this study |
| 33 | Royston district | Tr | Na, NaCa? | Seedorff, 1991 |
| 34 | Shamrock batholith | J | NaCa, Na | Battles, 1990; this study |
| 35 | Silver Dyke | K? | Na?, NaCa? | Kerr, 1936; this study |
| 36 | Simon quartz keratophyre | Tr? | Na | Knopf, 1921 |
| 37 | Yerington batholith | J | NaCa, Na | Carten, 1986; Dilles, 1984; Dilles et al., 1992; Dilles and Einaudi, 1992 |
| <i>OREGON</i> | | | | |
| 38 | Buck Creek tuff | J | Na | Dickinson, 1962 |
| 39 | Canyon Mtn. Complex | PTr | Na | Thayer, 1963, 1977 |
| 40 | Holbrook-Irondyke | P | Na | Vallier, 1967 |
| 41 | Oxbow | PTr | Na | Vallier, 1967 |
| 42 | Sparta district | PTr | Na, NaCa? | Gilluly, 1933 |

¹Age abbreviations: Dev = Devonian, J = Jurassic, K = Cretaceous, P = Permian, Pal = Paleozoic, Tr = Triassic²See Battles (1990) for a complete list of references

