TITLE: CHEMICAL CHANGES ASSOCIATED WITH ZEOLITIZATION OF THE TUFFACEOUS BEDS OF CALICO HILLS AT YUCCA MOUNTAIN, NEVADA

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ABSTRACT: The chemistry of the tuffaceous beds of Calico Hills was examined in samples collected over a 100 km² area south of the Timber Mountain-Oasis Valley caldera complex to determine regional geochemical patterns during zeolitization. Samples of 58 vitric and zeolitic tuffs were analyzed for 48 elements by a combination of x-ray fluorescence, atomic absorption spectrophotometry, and neutron activation analysis. Major and trace element concentrations for zeolitic tuffs vary significantly from those for vitric tuffs. Complex, geographically-controlled patterns of elemental enrichment and depletion in the zeolitic tuffs are found for Na, K, Ca, Mg, U, Rb, Sr, Ba and Cs. Vitric and zeolitic tuffs generally have the same SiO₂ contents on an anhydrous basis, but minor net silica gain or loss has occurred in some samples. Zeolitic tuffs from the northern part of the study area, adjacent to the caldera complex, are notably K-rich and Na- and U-poor compared to zeolitic tuffs to the south. The compositions of the K-rich zeolitic tuffs are similar to those found in other areas of the western US where volcanic rocks are affected by potassium metasomatism. Alteration of vitric tuffs took place in an open chemical system and geographic control of major element compositions probably reflects regional variations in groundwater chemistry during alteration. The K-rich zeolitic tuffs in the northern part of the study area were probably altered by hydrothermal fluids whereas tuffs further south were altered by lower-temperature groundwaters.

1 METHODS

Samples for this study were collected from four areas within a 100 km² region which encompasses most of the known outcrops of the tuffaceous beds of Calico Hills (Fig. 1). Samples of vitric tuffaceous beds of Calico Hills were collected from outcrops at Busted Butte in the southern part of the study area. Zeolitic tuffs were collected from outcrops of the same unit exposed at Prow Pass, located at the north end of Yucca Mountain, and Calico Hills, located at the north end of Jackass Flats. A total of 48 elements were determined in these vitric and zeolitic tuffs by a combination of x-ray fluorescence, atomic absorption spectrophotometry, and neutron activation analysis. Chemical data are available for the tuffaceous beds of Calico Hills penetrated by drill holes in the central part of Yucca Mountain (Broxton et al., 1986 and 1987). In the following discussions, these drill hole data are compared to the outcrop data collected in this study.

2 GEOLOGIC SETTING

The tuffaceous beds of Calico Hills is an informal stratigraphic unit within the southwest Nevada volcanic field and consists of intercalated nonwelded ash-flow tuffs, bedded ash-fall and reworked tuffs, and lava flows. These Miocene tuffs and lavas were erupted from rhyolite domes.
3 RESULTS

Elemental concentration in the following descriptions and figures are given on an anhydrous weight basis to facilitate comparisons between samples of variable water contents.

3.1 Vitric Tuffs at Busted Butte

Four samples of vitric tuffaceous beds of Calico Hills were collected from outcrops at Busted Butte. These tuffs are high-silica rhyolites characterized by 76.5% SiO₂, 4.80% K₂O, 2.80% Na₂O, and 0.85% CaO. Volcanic glasses within the tuffs are hydrated and whole-rock water contents average about 4% by weight. Trace elements concentrations, including U (4.8 ppm), Sr (50 ppm), Rb (200 ppm), and Ba (100 ppm), are typical of high-silica rhyolites throughout the southwest Nevada volcanic field (Broxton et al., 1989). Because of their low phenocryst contents (1-2%), whole rock compositions probably approximate compositions of glassy pyroclasts that make up the tuff.

Major- and trace-element compositions of the vitric tuff at Busted are nearly identical to those reported for vitrophyres associated with three Calico Hills lavas in Paintbrush Canyon (Broxton et al., 1989), located 14 km to the north (Fig. 1). Because of their similarities, data for the vitric tuffs and lavas are pooled for the discussion and the figures below.

3.2 Zeolitic tuffs at central Yucca Mt.

Chemical data for zeolitic tuffs at the site of the potential repository in central Yucca Mountain have been reported earlier (Broxton et al., 1986).
and 1987) and the results are briefly summarized here.
Alkali and alkaline earth compositions of zeolitic tuffs vary significantly from west to east across central Yucca Mountain. The zeolitic tuffs on the western side of central Yucca Mountain are relatively sodium-rich and are similar in composition to the vitric tuffs at Busted Butte (Fig. 2). In contrast, zeolitic tuffs on the eastern side of central Yucca Mountain contain less Na₂O and K₂O and more CaO relative to the vitric tuffs at Busted Butte (Fig. 2). Similar compositional patterns also occur in zeolitized tuffs found in deeper stratigraphic units in central Yucca Mountain (Broxton, et al., 1987).  

3.3 Zeolitic tuffs at Prow Pass  

The tuffaceous beds of Calico Hills at Prow Pass were studied in greater detail than other locations in this study because extensive outcrops provide an opportunity to examine vertical and lateral chemical variations in a relatively thick (100-120 m), thoroughly zeolitized unit. Altogether, twenty-one samples were collected in two vertical measured sections located 0.5 km apart. An additional 23 samples were collected in a lateral section that followed the northerly strike of the outcrop for a distance of about one kilometer.

The chemistry of the zeolitic tuffs at Prow Pass is distinctive when compared to the vitric tuffs at Busted Butte and the zeolitic tuffs at central Yucca Mountain. The zeolitized tuffs at Prow Pass are significantly more calcic (mean 2.07%) and less sodic (mean 1.11%) than the vitric tuffs at Busted Butte or the zeolitic tuffs in the western part of central Yucca Mountain. Potassium concentrations in the tuffs at Prow Pass are highly variable, ranging from 3.44% to 8.75% K₂O but tend to be greater (mean 5.47% K₂O) than the vitric or zeolitic tuffs to the south. Concentrations of mobile trace elements are highly variable, and although there is some overlap with concentrations found in the vitric tuffs, U, Sr, and Ba are mostly lower in the zeolitized tuffs at Prow Pass. Rb and Cs concentrations largely overlap those of the vitric tuffs but have a much wider range of values. Immobile elements such as Al₂O₃, TiO₂, Zr, Hf, and Th closely match those of the vitric tuffs at Busted Butte.
There is no consistent pattern of major-element variation with respect to vertical stratigraphic position in the vertical measured sections. Alkali and alkaline earth contents in these sections vary by up to 1 weight percent from sample to sample. K2O contents have an antithetic relationship with Na2O and CaO.

Although compositions are variable, tuffs sampled in the northern Prow Pass outcrops are more potassic and less sodic and siliceous than tuffs cropping out to the south (Fig. 3). Sr is more abundant in the southern part of the outcrop (Fig. 3). Sr concentrations are particularly elevated in the uppermost part of the southern outcrops where concentrations are as high as 742 ppm. Sample to sample element variability seems to be much greater in the southern part of the Prow Pass outcrops than to the north. For example, K2O contents vary by as much as 3 weight percent from sample to sample in the southern part of the traverse but are generally within 1 weight percent to the north.

3.3 Zeolitic tuffs at Calico Hills

Ten samples of zeolitized tuffaceous beds of Calico Hills were collected in a lateral traverse on the southwest side of Calico Hills (Fig. 1). These samples are significantly more potassic (5.4-9.4 wt.%, mean 7.6%) and less sodic (0.42-0.83 wt.%, mean 0.63%) than either the vitric tuffs at Busted Butte or any of the other zeolitic tuffs examined in this study (Fig. 2). Calcium concentrations are variable and, like the zeolitic tuffs at Prow Pass, many of the samples are calcium rich relative to the vitric tuffs. Magnesium is generally lower than in the vitric tuffs. Concentrations of mobile trace elements are highly variable with U, Cs, and Sr concentrations being generally less than vitric tuffs and zeolitic tuffs at central Yucca Mountain. Rb and Ba concentrations largely overlap those of the vitric tuffs but are significantly more variable in compositional range. Immobile-element concentrations for Al2O3, TiO2, Zr, Hf, and Th closely match those for vitric tuffs at Busted Butte. There are no systematic changes in major- or trace-element chemistry as a function of position along the lateral traverse.

4 DISCUSSION AND CONCLUSIONS

The close similarity between immobile major- and trace-element compositions from vitric tuffs at Busted Butte and zeolitic tuffs at central Yucca Mountain, Prow Pass, and Calico Hills indicates that the outcrop and subcrop samples examined in this study had similar whole rock compositions before diagenesis.
Elemental enrichment and depletion patterns in the zeolitic tuffs relative to the vitric tuffs reflect the mobilization and redistribution of Na, K, Ca, Mg, U, Rb, Sr, Ba, and Cs in the zeolitic tuffs by groundwater during alteration. Concentrations of Rb, Ba, and Cs in the zeolitic tuffs generally overlap those in the vitric tuffs. However, the larger compositional range for these elements suggests that they were also mobile during alteration. Silica concentrations are generally similar between the vitric tuffs and the zeolitic tuffs, however, minor amounts of silica depletion and silica enrichment have affected some of the samples.

The degree of elemental enrichment and depletion is greatest in the northern zeolitic tuffs and probably reflects more severe alteration conditions in areas proximal to the TM-OV caldera complex than to the south. The Calico Hills is part of a large area affected by regional hydrothermal alteration during the waning stages of volcanism at the TM-OV complex from 10-11.5 Ma (McKay, 1963; Jackson et al., 1988). Geochromically, this hydrothermal alteration is manifested by significant potassium enrichment and by sodium and uranium depletion. Potassium contents in the altered tuffs are similar to those found in volcanic rocks affected by potassium metasomatism in other hydrothermally-altered areas of the western US (Chapin and Lindley, 1986).

The formation of K-rich zeolitic tuffs may represent an important stage in the development of K-metasomatism in volcanic terranes elsewhere. Typically, K-metasomatism results in the pervasive replacement of host rocks by adularia + hematite ± quartz ± illite-montmorillonite. Preliminary petrographic, x-ray diffraction, and microprobe data indicate that the mineral assemblage at Calico Hills includes felspar + mordenite + quartz + opal ± clinoptilolite ± kaolinite ± calcite. Potassium in the altered tuffs at Calico Hills is passed from successive secondary minerals in the paragenetic sequence of clinoptilolite → mordenite → adularia. The differences between the mineral assemblages at Calico Hills and at other K-rich metasomatic terranes probably reflect lower temperatures of the hydrothermal fluids at Calico Hills.

The presence of zeolites during the early stages of alteration probably facilitated the introduction of K into the rock system because of the high selectivity for potassium during clinoptilolite crystallization and because of the ease with which ion-exchange occurs between zeolites and fluids they are in contact with. Also, these nonwelded tuffs were probably highly permeable during the early stages of alteration, but became increasingly impermeable as zeolitization progressed. Therefore, it seems likely that the K-rich zeolitic tuffs reflect the presence of K-rich groundwaters during the initial stages of alteration.

Although the zeolitized tuffs at Prow Pass have not been previously described as being hydrothermally altered, these rocks have many of the same chemical and mineralogic characteristics as the tuffs at Calico Hills. Therefore, it seems probable that these tuffs were also altered under hydrothermal conditions. The somewhat lower K2O contents in these rocks probably reflect groundwaters that were less potassic and perhaps somewhat cooler than those at Calico Hills. The northward increase in K contents in these tuffs suggest that the focus of hydrothermal alteration was located in that direction. This interpretation is supported by other studies that show that alteration becomes more pronounced northward in the Yucca Mountain region and that alteration was largely driven by the large thermal anomaly associated with the development of the TM-OV caldera complex (Bish, 1987; Broxton et al., 1987).
The compositions of zeolitic tuffs from the western portion of central Yucca Mountain are very similar to those found in vitric tuffs and probably reflect relatively low alteration temperatures compared to Calico Hills or Prow Pass. This is supported by the dominance of clinoptilolite, which is stable only at relatively low temperatures, as the primary alteration mineral and by the much lower abundance of adularia in these tuffs. Groundwaters were probably a Na-K bicarbonate type which is typical of tuff aquifers in the region (Winograd and Thordarson, 1975). Processes responsible for the development of calcic zeolitic tuffs on the eastern side of central Yucca Mountain are poorly understood at this time but may reflect cation exchange of zeolites with groundwaters partially derived from underlying Paleozoic aquifers (Broxton et al., 1987). These calcic tuffs are the subject of additional study.

CONCLUSIONS

Alteration of the tuffaceous beds of Calico Hills in the Yucca Mountain region took place in an open chemical system and resulted in significant rearrangement of mobile cations during diagenesis. Geographic variations in the chemistry of zeolitic tuffs probably reflect regional differences in groundwater chemistry during alteration. In part, differences in regional groundwater chemistry probably reflect widespread hydrothermal activity in areas marginal to the TM-OV caldera complex.

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REFERENCES


