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POTASSIUM METASOMATISM OF VOLCANIC AND SEDIMENTARY ROCKS IN RIFT BASINS, CALDERAS, AND DETACHMENT TERRANES. Chapin, C. E., New Mexico Bureau of Mines and Mineral Resources, Socorro, NM 87801 and Lindley, J. I., Department of Geology, University of North Carolina, Chapel Hill, NC 27514

Potassium metasomatism of volcanic and sedimentary rocks is a common type of alteration in areas of regional extension. The alteration is chemically and mineralogically distinctive but is visually subtle and easily overlooked in outcrop and thin section. In highly metasomatized volcanic rocks, K_2O is as high as 13.5 wt. % and Na_2O, CaO, and MgO are each commonly less than 1 wt. %. Metasomatism tends to homogenize volcanic rocks of diverse composition to a mixture of K-feldspar (adularia) + hematite ± quartz ± illite-montmorillonite, yet rock textures are faithfully preserved. Potassium-bearing phenocrysts, such as sanidine and biotite, are little affected and give the illusion that the rocks are fresh.

In this paper, we describe the chemical, mineralogical, and oxygen-isotopic changes accompanying K-metasomatism and point out the similarities with diagenetic reactions in both deep marine and alkaline, saline-lake environments. The common occurrence of K-metasomatism in upper-plate rocks of detachment terranes indicates that the early stage of severe regional extension causes crustal downwarping and, in arid to semi-arid regions, development of closed hydrographic basins.

Our data come mainly from detailed studies of K-metasomatism in the Socorro area of the Rio Grande rift, especially studies by Lindley (1; 2) and D'Andrea (3). The Socorro area affords an unusual opportunity to study K-metasomatism because five regional ash-flow tuff sheets extend across the potassium anomaly and well beyond it. Thus, sample traverses can be made from fresh rock into progressively more altered rock within the same stratigraphic unit. The interbedding of basaltic andesite lavas between the ash-flow sheets allows examination of alteration effects on both mafic and silicic rocks. Alteration of overlying early rift fanglomerates permits analysis of clasts of different rock types within the same small volume of rock. Stratigraphic relationships and correlations have been established during more than 30 thesis and mapping projects over the past 15 years; the results are summarized in Osburn and Chapin (4).

The most important feature of the Socorro potassium anomaly is its large size. An L-shaped area 40 to 50 km on a side and at least 20 km in width has been outlined by analysis of more than 200 samples of ash-flow tuffs. Unaltered tuffs outside the anomaly average 5.1% K_2O; the same stratigraphic units within the anomaly average 8.0% K_2O, with K_2O ranging as high as 10.4%. The tuffs average 500 m in cumulative stratigraphic thickness; their volume within the potassium anomaly is approximately 900 km^3. Limited data indicate that interbedded basaltic andesite lavas are much less affected and show an erratic distribution of alteration. Clasts of both tuffs and mafic lavas in early-rift fanglomerates are highly altered with K_2O contents as high as 11.6%. Using only the volume of altered tuffs (900 km^3) and an average enrichment of 2.9% K_2O, a minimum of 6.4×10^{10} tons of potassium (K) have been added! The magnitude of this figure and the size of the area affected impose important constraints on the origin of the alteration.

One arm of the L-shaped potassium anomaly at Socorro trends northward along the axis of the early rift Popotosa basin. Late-rift (<10 Ma) block faulting has exposed pervasively metasomatized ash-flow tuffs overlain by early-rift clastic sedimentary rocks and by as much as 300 m of fine-grained playa deposits. Crustal extension along the basin axis has been estimated by Chamberlin (5) to be 200 ± 50%. The other arm of the Socorro potassium anomaly extends about 50 km southwest from Socorro across an overlapping series of late Oligocene calderas that were downwarped beneath the Popotosa basin as they underwent extension of 30 to 200%. K-metasomatism is restricted to the stratigraphic interval between the first major ash-flow sheet (the 32.0 Ma Hells Mesa Tuff) and an as yet undefined level within sedimentary deposits of the Miocene Popotosa basin. Lateral boundaries vary from relatively sharp (<2 km), cross-cutting both structural grain and stratigraphic boundaries, to relatively diffuse with marked stratigraphic control. Permeability and composition of stratigraphic units were major vertical controls of K-metasomatism; lateral controls were permeability, salinity, and possibly temperature of altering fluids.

Chemically, the alteration is distinctive. As K_2O increases, Na_2O and CaO decrease. Total alkali content increases by 1 to 2% in welded tuffs and by as much as 5% in mafic lavas (6). Clasts of mafic lavas in early rift fanglomerates show the most extreme metasomatism, perhaps because of their reactive composition and location in permeable, silica-rich basin sediments. K_2O/Na_2O ratios for unaltered ash-flow tuffs outside the anomaly average 1.2; the same stratigraphic units within the anomaly have K_2O/Na_2O ratios as high as 42.1. Unaltered basaltic andesite lavas outside the anomaly have an average K_2O/Na_2O ratio of 0.7; similar lavas within the anomaly have K_2O/Na_2O ratios as high as 35.0. Thus, the K_2O/Na_2O ratio provides a sensitive index useful in scanning lists of chemical analyses for signs of K-metasomatism.

Other chemical changes accompanying K-metasomatism in the Socorro area are increases in Rb and Ba and decreases in Sr, Mn, and MgO (3; 6). The Fe^{+3}/total Fe ratio increases markedly in mafic to intermediate rocks but remains relatively unchanged in rhyolitic tuffs, probably because of the higher initial oxidation state of the tuffs. TiO_2, total Fe, Zr, Y, Th, and U remain unchanged (3; 6). Agron and Bentor (7) describe very similar chemical and mineralogical changes in K-metasomatized Precambrian rhyolites bordering the Dead Sea rift. Glazner (8) reports similar changes in K-metasomatized volcanic and sedimentary rocks of the Cady Mountains, Mojave Desert, California. Both studies determined that rare earth elements were essentially immobile during metasomatism.

Mineralogically, K-metasomatism is characterized by pervasive replacement of diverse rock types by K-feldspar (adularia) + hematite ± quartz ± illite-montmorillonite (2). In ash-flow tuffs, groundmass tridymite and cristobalite recrystallize to low quartz (2). Phenocrystic plagioclase is replaced by a fine-grained, intimate mixture of approximately equal amounts of adularia and quartz (2). Groundmass plagioclase undergoes patchy replacement by adularia. Phenocrystic quartz, sanidine, and biotite typically remain unaffected.

With extreme alteration, groundmass quartz and phenocrystic sodic sanidine are also replaced by adularia (2). In basaltic andesite lavas, groundmass plagioclase is replaced by adularia and both phenocrystic and groundmass pyroxene are converted to hematite (2). Groundmass magnetite is also hematized. The first visible sign of alteration in hand samples of either rock type is a chalky appearance of plagioclase; the first sign in thin section is patchy replacement of plagioclase by adularia.

The secondary K-feldspar is very pure (Or 96 to 100), contains 15.8 to 16.3 wt. % K_2O, is monoclinic, and has a slightly ordered structural state approaching that of orthoclase (2). This secondary feldspar is fine grained (20 microns) and has the rhombohedral habit characteristic of diagenetic/hydrothermal adularia (2). In altered phenocrystic plagioclase, where adularia is intimately associated with fine-grained quartz, the two minerals are coprecipitated in a chaotic manner, beginning along cleavages. This results in creation of void spaces which imparts a secondary porosity and decreases rock density (9).

Isotopically, $\delta^{18}O$ increases in rhyolitic tuffs from values of +8 to +10 permil, typical of unaltered rock, to +11 to +13 permil, typical of altered rock (2). Secondary K-feldspar has a minimum $\delta^{18}O$ of +12.7 permil and secondary quartz has an estimated minimum $\delta^{18}O$ of +15.4 permil (2). Phenocrystic quartz and sanidine retain their magmatic values of approximately +8 and +7 permil, respectively. In contrast to the rhyolitic units, basaltic andesite lavas become isotopically lighter with metasomatism. Unaltered mafic lavas, have ^{18}O values of approximately +9 permil compared to +6 permil in altered lavas (2). The strong tendency of iron oxides to concentrate light oxygen (10) and the alteration of abundant pyroxene to hematite in the altered lavas may be responsible.

Previous interpretations of K-metasomatism have been in terms of fossil geothermal systems (11; 6; 7; 8). Chapin and Glazner (12) listed 14 areas in the southwestern United States where K-metasomatism is known and pointed out that in all these areas the upper crust has been severely disrupted by regional extension, caldera collapse, or both. The association seems to be with areas of high heat flow and severely fractured crust. The Biq'at Hayareah area in the Sinai-Negev Desert, studied by Agron and Bentor (7), also displays this association. There the volcanic rocks dip 25° to 90° and are situated on the margin of the Dead Sea rift.

In a recent study of discordant K-Ar and fission-track ages of upper-plate volcanic rocks associated with the Harcuvar Mountains detachment terrane in western Arizona, Brooks and Marvin (13) suggest that K-metasomatism occurred at temperatures greater than the $\sim$200°C annealing temperature of fission tracks in zircon. Kerrich and others (14) report that K-metasomatized upper-plate rocks in the nearby Picacho detachment terrane are oxidized and $\delta^{18}O$ enriched, as are the rocks at Socorro, and postulate that alteration occurred during expulsion of metamorphic fluids from the lower plates at temperatures less than 300°C. The $\delta^{18}O$ values of K-metasomatized rocks at Socorro can be interpreted as indicating either equilibration with waters enriched in heavy oxygen (+5 to +10 permil) at temperatures of 250° to 350°C or reaction with meteoric waters at temperatures of 30° to 80°C (2). An independent measure of paleotemperature is needed at Socorro. However, geologic evidence and data from the literature on diagenetic reactions in both deep-marine and alkaline, saline-lake environments strongly favor a relatively low-temperature regime.

Diagenetic changes in sea-floor sediments and volcanic rocks have been well documented by studies arising from the Deep Sea Drilling Project. Mellis (15) and Mathews (16; 17) discovered early on that calcic cores of plagioclase phenocrysts in deep-sea basalts were replaced by water-clear K-feldspar similar to orthoclase. Since then, numerous studies of sea-floor diagenesis have documented that basalts typically gain K, Rb, Ba, Cs, $\delta^{18}O$, and Fe^{+3}/total Fe and lose Ca, Mg, Na, Sr, and Mn to the pore waters (see for example 17; 18; 19; 20; 21). Most of the ions removed are taken up in secondary minerals such as Ca in calcite and Mg in smectites. The mobility of some ions is strongly temperature-dependent, but most alteration of sea-floor basalts occurs at temperatures less than 100°C and the results are rather uniform over large areas of the ocean floor (20). Bloch and Bischoff (22) have shown that when saline fluids react with basaltic rocks at low temperatures potassium is fixed, while at temperatures above 150°C sodium is fixed. Munha' et al. (23) report that sea-floor rhyolites show strong enrichment in potassium, development of an adularia-quartz-hematite assemblage, depletion in Na, Ca, Mg, Mn, and Zn, and enrichment in heavy oxygen. These changes are strikingly similar to potassium metasomatism at Socorro.

Even more relevant, however, are studies by Hay (24, 25), Sheppard and Gude (26; 27; 28; 29) and Surdam and Sheppard (30) which have shown that silicic vitric tuffs interbedded in sediments of alkaline, saline lakes can be progressively altered basinward through a sequence of zeolites to K-feldspar. The diagenetic reactions occur rapidly in a low-temperature, near-surface environment. Increased alkalinity and salinity drives the reactions toward the anhydrous phase. An alkaline, saline environment at Socorro is indicated by abundant zeolites (clinoptilolite, mordenite, analcite) and gypsum in the playa deposits of the Popotosa basin, as well as traces of halite and anomalous lithium content of ash beds (31). Popotosa fanglomerates and sandstones are reddish brown and extremely well indurated within the potassium anomaly, but are buff colored and only moderately indurated outside the anomaly. Reddish coloration and unusually strong induration are typical of coarse clastic rocks in other areas of K-metasomatism, including upper plates of detachment terranes.

The oldest sedimentary deposits of the Popotosa basin have been dated at about 26 Ma (32); the basin persisted as a broad (60-km-wide), shallow, closed hydrographic entity until about 7 Ma when Basin and Range faulting broke the basin into a series of three narrow basins with intervening ranges. Thus, as much as 19 m.y. was available for downward percolation of alkaline, saline waters into permeable volcanic and sedimentary units beneath the basin floor. Closely spaced, domino-style normal faults and strong rotation of beds accompanying severe extension of the basin floor may have aided the downward migration of saline waters. The great areal extent of the K-metasomatism (1800 km^2), its subtle nature, simple mineral assemblage, enrichment in heavy oxygen, and location in a rift basin argue strongly for a diagenetic rather than hydrothermal origin.

Increased temperature also drives zeolitic reactions towards the anhydrous feldspar end members (33). Maximum depth of burial of K-metasomatized rocks at Socorro was approximately 1.8 km. Reasonable temperature estimates at this depth vary from 74°C (heat flow 80 mw/m^2) to 92°C (heat flow 107 mw/m^2) depending on whether an intermediate or high heat flow is assumed (average Basin and Range heat flow is 89 mw/m^2). Thus, temperature was probably not the dominant factor causing K-metasomatism at Socorro. Elevated temperatures may have played a more important role in K-metasomatism in calderas such as the Bachelor Mountain caldera, San Juan volcanic field, Colorado, where Ratte' and Steven (34) discovered a 10 x 16-km potassium anomaly. However, the adjacent and slightly younger Creede caldera (26.5 Ma) hosted an alkaline, saline-lake system in which lacustrine sediments underwent diagenetic reactions to clays, zeolites, and moderately abundant K-feldspar (35) without evidence of significant temperature control. The subtle nature of K-metasomatism and lack of conspicuously altered zones, such as occur where convecting geothermal waters are channelized along permeable pathways, indicates that the thermal gradient during K-metasomatism was less than that required for hydrothermal convection (36).

The initial response of continental lithosphere to thinning by regional extension is downwarping to form broad, shallow depressions. Isostacy requires this response and numerous studies of continental rifts have documented it in spite of the widely held misconception of early doming (37). The detachment terranes of the southwestern United States are located in an area which has had an arid to semi-arid climate throughout much of Cenozoic time. Subsidence in such a setting should lead to formation of closed hydrographic basins and development of alkaline, saline lakes. The widespread occurrence of K-metasomatized volcanic rocks in the upper plates of detachment terranes, together with the nearly ubiquitous presence of reddish-brown, highly indurated clastic sedimentary rocks interbedded with upper-plate volcanic units, indicates that early stages of detachment faulting produce subsidence. At Socorro, the subsidence stage lasted for nearly 20 m.y. (26-7 Ma) and was followed by uplift and block faulting in typical Basin and Range style. The preservation of upper-plate rocks and detachment surfaces in many ranges of the Basin and Range province also indicates that uplift was a late-stage event. We suggest that the term "metamorphic core complex", with its implications of domal uplift, is a misnomer. Such complexes are merely exposures of planar or gently curved, low-angle detachment surfaces that spent most of their existence beneath broad downwarps which, in arid climates, contained closed hydrographic basins.

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