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AGE OF ADULARIA AND METAMORPHISM, OUACHITA MOUNTAINS, ARKANSAS

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ABSTRACT. Adularias from quartz veins in the Ouachita Mountains give isotopic ages that bracket the time of crystallization between 287 and 214 m. y. ago. A Middle Pennsylvanian age is excluded. Combined isotopic, stratigraphic, and structural data suggest deposition in Late Pennsylvanian or Early Permian time and persistence of mild deformation and elevated temperatures related to low-grade regional metamorphism into and possibly somewhat after Middle Permian time. The metamorphism may coincide with a 250-m. y. heating event in the southern Appalachian area.

Feldspars either highly ordered or highly disordered with respect to Al-Si distribution lose Ar at low temperature to extents that apparently do not differ significantly. The data suggest continuous diffusional loss activated by very slow Al-Si ordering toward the stable structural state of maximum microcline. Feldspars in intermediate structural states are more prone to such ordering and give lower ages.

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Quartz veins in the Ouachita Mountains, Arkansas, best known for the excellent quartz crystals they have yielded, occupy fissures in rocks ranging in age from Ordovician or possibly Cambrian to Pennsylvanian (Engel, 1951, p. 186-187; Flawn and others, 1961, p. 25-26). The mineralogies of most veins faithfully reflect the compositions of enclosing wall rocks, suggesting that some or all major elements of certain vein minerals were derived by lateral secretion from adjacent wall rocks (Engel, 1951, p. 232-233). The veins are thus typical of those in unmetamorphosed and low-grade metamorphic rocks (Holmquist, 1921, p. 615-623). Adularia-bearing veins are found in shale and to a lesser extent in argillaceous sandstone (Engel, 1951, p. 227) and resemble some adularia-bearing Alpine cleft veins. Chlorite as a vein constituent is restricted to shales and is especially common in veins in the relatively MgO-rich, tuffaceous Stanley shale (Engel, 1951, p. 229, 233).

DATED SPECIMENS

The two dated specimens are from the Hamilton Hill locality, Garland County (Engel, 1951, pl. 25, loc. 2; pl. 38), and resemble an illustrated specimen (1951, pl. 33B) collected about 600 feet west northwest of the dated specimens.

Specimen 1 is a breccia of angular to subangular fragments of Early(?) to Middle Ordovician Womble shale (Flawn and others, 1961, p. 27) cemented by subequal amounts of quartz and adularia. Typically the Womble in this area is a black shale with slaty cleavage, but the breccia fragments are weathered to a soft residue, mottled or streaked by ochre and brown, with scattered black-coated joints and weathering pits. The fragments are massive or vaguely laminated, the lamination being probably a relict of the slaty cleavage. Adularia forms vein margins (Engel, 1951, p. 277). It coats the shale fragments and is the sole major mineral of smaller fissure fillings. On fresh fractures it is white and light pink, the pink occurring as distinct irregular patches in relatively massive areas of feldspar. Quartz forms masses up to more than one inch across in the centers of larger veins. Intergrowth of quartz and feldspar is quite limited, and in only one place was quartz seen in apparent contact with shale. The larger fissures are incompletely filled, leaving irregular vugs lined by terminated, small (about one-eighth inch) wedges and rhombs of adularia and prisms of quartz up to seven-eighths inch long. Well terminated adularia is all white. Both adularia and quartz may be coated with red iron oxide and clay along joints and in vugs.

Specimen 2 is a mixture of coarse terminated quartz and adularia taken from a large vug. The adularia is in crudely bladed crystals often grouped to give a coxcomb effect. $\delta O^{18}/O^{16}$ values for this specimen are as follows (Epstein and Taylor, 1967, p. 56-58; δ values relative to standard mean ocean water, SMOW): quartz, +18.3; feldspar, +15.3. The isotopic fractionation indicates a temperature of 250°C, from which a $\delta O^{18}/O^{16}$ of +8.0 for the water in the vein-forming solution is calculated.

For Rb-Sr dating the whitest, cleanest adularia rhombs were hand picked from a single vug in specimen 1 and crushed to −115 mesh. The subordinate material with a surface coating of iron oxide or clay, presumably from the outer surfaces and cracks of the crystals, was easily removed in a Frantz isodynamic separator so that the material dated is essentially a pure feldspar representing almost the whole mineral. X-ray diffraction indicates pure K-feldspar, almost monoclinic, but with a slight broadening of (130) and (131) peaks indicating partial ordering to a form with low triclinicity (Goldsmith and Laves, 1954).

Both specimens were dated by the K-Ar method. From specimen 1 large pieces of vein were crushed to −32,+50 mesh and separated into three density fractions of which the least magnetic portions were selected and further cleaned by hand-picking any pieces with distinct stains or coatings. X-ray analysis shows that the least dense fraction, which is largely opaque and has a cream-colored to pink cast, is microcline with high but not quite maximum triclinicity. The densest fraction is white, transparent to opaque, and gives slightly broadened peaks indicating low triclinicity, quite like the sample used for Rb-Sr dating. The intermediate fraction gives peaks indicating a mixture of the other two with little evidence for a significant range of triclinicities in either. Thus, the pink and white feldspars of specimen 1 are distinct crystallographically as well as in color, due either to primary differences inherited from a complex history of vein deposition or to much later differential Al-Si ordering controlled perhaps by slight compositional or initial structural differences. If the triclinic forms are secondarily ordered from primary monoclinic adularia, as suggested by Chaisson (1950), those fractions with higher triclinicity should lose more argon and give lower ages. As shown later, such is not the case. If the differences are primary, as seems likely, they offer a means of comparing argon retentivity in K-feldspar as a function of structural state. The discussion will follow this line. The lightest and densest fractions were dated but not the intermediate.

From specimen 2 large crystals were crushed to −10, +32 mesh, cleaned by hand-picking, and separated into two density fractions. The density contrast is faint. Only the denser fraction was dated. It is the most sharply monoclinic feldspar of all. The less dense fraction is monoclinic to all intents and purposes but shows a distinct loss of relative peak heights of (130) and (131) and a barely detectable broadening of (131) compared to the denser fraction.

It may be noted that in both specimens the more ordered feldspar is less dense, which is contrary to expectation from general crystal structural considerations and from the typically higher refractive indices of more ordered forms. The less dense ordered form from specimen 1 is pink, so hematite content is not the explanation. The density difference must lie in Na content, trace element content, second order decrease of density due to domain boundaries in twinned triclinic crystals, or dense inclusions.

Rb-Sr AGE

Results are shown in table 1. The analytical uncertainty is about 3 percent. Feldspars retain radiogenic Sr very well in general, so the main uncertainty in the age is the initial Sr^{87}/Sr^{86}. The 287 m. y. age, calculated assuming this ratio is 0.704, is a probable maximum and by the most recently proposed time scale (Kulp, 1961) is Late Pennsylvanian. The 279 m. y. age was calculated using an initial ratio of 0.709, which would prevail if Sr similar to that in sea water was released from limestones and swamped all other Sr in the vein-forming solutions. This age is on the Pennsylvanian-Permian boundary. It is possible that the initial ratio was even higher, stemming from an old siliceous basement like that in Missouri, Oklahoma, and Texas, or from the Womble shale wall rock itself which may have inherited radiogenic Sr at the time of deposition and was about 200 m. y. old when the veins were formed. In order for the apparent age to be as low as 250 m. y. (Middle Permian), which is the age of an apparently widespread heating event in the southern Appalachian area (Kulp and Eckelmann, 1961), the initial ratio would have to be 0.724. The likelihood of this value is unknown, but it is tentatively concluded that the adularia probably crystallized during the Late Pennsylvanian or Early Permian epoch and that a lateral secretion origin, which may hold for major elements, does not hold for all trace elements and isotopic species. This is supported by evidence for active upward flow of vein-forming solutions (Engel, 1948; 1951, p. 220-225, 233-235) which would allow mixing of distantly derived elements.

TABLE 1

Rb-Sr data, white feldspar of low triclinicity, specimen 1

Rb, ppm	Com, Sr, ppm	Sr^{87}/Sr^{86}*	Assumed initial Sr^{87}/Sr^{86}	Radiogenic Sr^{87}, ppm	Age, m. y.**
279.2	18.01	0.8834	0.704	0.3161	287
			0.709	0.3074	279

* Normalized to $Sr^{86/88} = 0.1194$ (atomic ratio); measured in unspiked run.
** $\lambda = 1.39 \times 10^{-11}$/yr.

The problem could be precisely resolved by isotopic analysis of adularia and a contemporaneously deposited Rb-poor phase such as calcite. C. Milton (personal commun., 1967) was unable to find a mixed adularia-calcite vein among many hundred samples examined. The K-Ar dating was undertaken to help resolve the problem.

K-Ar AGES

Cretaceous and younger sanidines from tuffs are known to give ages that are reliable as judged by those of coexisting biotites, whereas older feldspars give ages of variable reliability (Asklund, Baadsgaard, and Folinsbee, 1961; Smith and others, 1961; Folinsbee, Baadsgaard, and Lipson, 1960; McDougall, 1961). Feldspars are not usually subject to Ar inheritance problems, especially in shallow veins and tuffs, so the K-Ar ages set a younger limit on the adularias and perhaps on the Ouachita metamorphism. The results are given in table 2. Analytical uncertainties are about 3 percent. The limit is set by the 214 m. y. age of the monoclinic feldspar from specimen 2, which is about Middle Triassic (Kulp, 1961). Elevated temperatures attending the metamorphism did not persist beyond this time. This limit is younger than any yet postulated by geologists working in the area, and it is probable that all three feldspars suffered Ar loss. The cause is not obvious. No young dikes are known in the immediate area. Clearly visible hydrothermal alteration and weathering effects were avoided for the most part and minimized by hand-picking where seen.

TABLE 2

Specimen	Triclinicity	K, wt%*	Radiogenic Ar^{40}, cc STP/g K	Radiogenic Ar^{40}, %	Age, m. y.**
1	High	12.82	8.63×10^{-4}	77.1	205 ± 6
1	Low	12.89	7.97×10^{-4}	88.1	190 ± 5
2	Zero (Monoclinic)	12.53	9.03×10^{-4}	92.4	214 ± 6

* Perkin-Elmer flame photometer, Li internal standard.

** $\lambda_\beta = 4.72 \times 10^{-10}$/yr.; $\lambda_K = 0.584 \times 10^{-10}$/yr.

The post-Paleozoic history of the feldspars probably involved temperatures at no time significantly above those at the Earth's surface or at shallow depth, so loss by volume diffusion is insignificant (Fechtig and Kalbitzer, 1966, p. 101, 106-107). Accelerated diffusion due to perthitic exsolution cannot be excluded, but the X-ray patterns indicate absolutely no albite, and this cause is probably unimportant. If it were, it should cause preferential loss from the feldspar of high triclinicity, which would be expected to show the greatest exsolution, or from the monoclinic feldspar which has the lowest K content, hence presumably the highest Na content. Yet these feldspars give the higher ages. The cause of loss is probably a second order effect other than those discussed above—probably some discrete lattice process that is perhaps best identified by examining the age discrepancies among the three feldspars.

The monoclinic feldspar gives the highest age in accord with the conclusion of Fechtig and Kalbitzer (1966, p. 93), and many others before them, that sanidine is the best feldspar for K-Ar dating. However, such studies generally involved a comparison of "sanidine" and "microcline" without examining the effects of varying structural state which may account for some of the discrepancies in measured diffusion constants. These studies predict that the highly triclinic feldspar will give the lowest age if the structural ordering occurred long after crystallization. The difference in ages of the monoclinic and highly triclinic feldspars is at most marginally significant, so the ordering of the triclinic feldspar probably occurred primarily during vein formation. Clearly, if the structural states remain unchanged, extreme differences of structural state do not alone account for the age discrepancies.

The white feldspar of low triclinicity from specimen 1 gives a significantly lower age than the other two. Both it and the monoclinic feldspar are exposed in vugs, so differential exposure to flowing hydrothermal or ground water is not the answer. The white feldspar has much more transparent material than the uniformly opaque triclinic feldspar from the same specimen, so alteration is evidently not the cause. It may lie in something inherent in intermediate as opposed to highly ordered or disordered structures. Gubser and Laves (1967, p. 187) suggest that adularia orders through geologic time toward the stable structural state of maximum microcline. But the extent of spontaneous Al-Si ordering at low temperature is uncertain and most likely small. Any (post-Triassic) ordering in the monoclinic feldspar is below the limits detectable by the simple powder diffractometry used; but, granting some finite ordering, feldspars of intermediate structural state may have a lower inherent metastability against it. To summarize, the suggested cause of Ar loss is diffusion activated by low-temperature Al-Si ordering, and discrepancies in loss are due to the greater tendency for feldspars in intermediate states to undergo further ordering. In this respect it would be of interest to compare the argon retentivities of different parts of adularia crystals zoned with respect to structural state. This would virtually assure identity of true age and absence of differences in pressure, temperature, and alteration histories and would allow isolation of lattice-dependent effects.

A likely history permitted by the isotopic data is that the adularias were deposited in Late Pennsylvanian or Early Permian time, metamorphism and elevated temperatures persisted through Middle Permian time (the 250-m. y. event of the southern Appalachian area), and slight diffusional Ar loss in post-Middle Permain time controlled the apparent 214 m. y. age which sets a younger time limit on these events.

STRATIGRAPHIC AND STRUCTURAL AGE LIMITS ON VEINS

In the subsurface extension of the Ouachita structural belt in Texas, both pre- and post-deformation quartz and carbonate veins are known (Flawn and others, 1961, p. 77-79, 118). In the exposed rocks of the Ouachita Mountains proper only one generation of veins has been defined. These veins are localized in fractures related to folding of Paleozoic rocks, and the major quartz deposits are concentrated in the zone of most intense (though still low-grade) metamorphism (Engel, 1951, p. 243). The youngest, folded, vein-bearing rocks are Atoka (Engel, 1951, p. 186-187) of Early to early Middle Pennsylvanian age (Flawn and others, 1961, p. 40). The veins are not folded but are faulted, fractured, crushed, and sheared; broken or displaced quartz crystals are healed or overgrown (Miser, 1943, p. 98-99; Engel, 1951, p. 235-237). Conglomerates in the Paleozoic sequence, including Pennsylvanian conglomerates, have few or no clasts of vein quartz (Miser, 1943, p. 100). Lower and upper Cretaceous rocks unconformably overlie the Paleozoic rocks near the Ouachita Mountains and are not cut by quartz veins, but Cretaceous gravels contain abundant locally derived quartz clasts, and Cretaceous igneous dikes are known to cut quartz veins (Miser, 1943, p. 100, 113).

The veins are thus Middle Pennsylvanian or younger and probably pre-Cretaceous. They were deposited during the late stages of a deformational event as indicated by fracturing without folding and before the termination of hydrothermal activity and perhaps of metamorphism.

Waterschoot van der Gracht (1931, p. 1027-1029) suggests that the orogeny extended into Permian time. However, most early workers date the deformation as Middle Pennsylvanian (Engel, 1951, p. 243), and Miser (1943, p. 98-99, 117) concludes from this and the absence of evidence for post-Pennsylvanian deformation that the veins were emplaced at the end of Middle Pennsylvanian time.

The authors of the latest summary work on the Ouachita system (Flawn and others, 1961) generally favor a Middle Pennsylvanian deformation, but Goldstein (Flawn and others, 1961, p. 44) and King (Flawn and others, 1961, p. 187-188) would allow movements, perhaps reduced in intensity, to persist to the end of Pennsylvanian time. Early Permian deformation is known in the Marathon region, Texas, and in northeastern Mexico, and one might infer that deformation persisted into Permian time in the Ouachita Mountains where the absence of upper Pennsylvanian and Permian rocks does not allow setting an upper stratigraphic limit. Flawn (Flawn and others, 1961, p. 124-127) is the strongest advocate of termination of deformation in Middle Pennsylvanian time. He bases this on the lack of deformation and metamorphism of the middle to upper Pennsylvanian Morehouse Formation, in contrast to the deformation and metamorphism of middle Pennsylvanian rocks of the Ouachita Mountains. The Morehouse Formation is known only south of the mountains in the subsurface section of a single well in Morehouse Parish, Louisiana. The formation was not entirely penetrated. Imlay and Williams (1942) raise the possibility that the Morehouse rests on a resistant block and was buttressed against the effects seen in the Ouachita Mountains. This explanation gains credence in view of increasing evidence for a Permo-Carboniferous episode of rifting and continental drift (Irving, 1966) and for which there is specific evidence in the Ouachita region (Muehlberger, 1965; Bass, in preparation).

The Ouachita Mountains are hereby viewed as underlain by the deformed contents of a Carboniferous rift basin to which metamorphic effects were restricted. Such effects may have persisted into Permian time.

CONCLUSION

The adularia-bearing quartz veins are not as old as Middle Pennsylvanian. The combined isotopic, stratigraphic, and structural data indicate that the veins were deposited in Late Pennsylvanian or Early Permian time and allow that metamorphism and the mild terminal effects of deformation persisted into Middle Permian time and possibly somewhat longer.

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