Al₂SiO₅ MINERALS IN ROCKS OF THE SIERRA NEVADA AND INYO MOUNTAINS, CALIFORNIA[1]

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Abstract

The regional occurrence of andalusite in metamorphic rocks of the Sierra Nevada and Inyo Mountains indicates that the maximum total pressure that the rocks have been subjected to was at or below the upper pressure limit of andalusite stability. Sillimanite is a contact metamorphic mineral and is generally restricted to metamorphic rocks associated with the older granitic rocks of the Sierra Nevada batholith, which predate the Late Cretaceous. Kyanite was found in a sample of stream sediment at one locality in the western Sierra Nevada; however, its source is unknown.

Four samples each of purified andalusites and sillimanites, including two coexistent mineral pairs, were spectrographically analyzed for trace elements, and major elements were determined for seven of the separates. Consistent partitioning patterns of certain trace elements between andalusites and sillimanites suggest that foreign-ion stabilization may play a role in survival of the polymorphs.

Introduction

All three polymorphs of Al₂SiO₅, andalusite, sillimanite, and kyanite, have been reported in rocks from the Sierra Nevada. Several occurrences of these minerals in the central Sierra Nevada and Inyo Mountains have been studied, as part of a continuing investigation of processes responsible for formation of the Sierra Nevada batholith. In addition to examination of Al₂SiO₅-bearing rocks, particular attention has been given to composition of the alumino-silicate minerals. The need for reliable compositional data on natural Al₂SiO₅ phases has recently been emphasized by several workers (*e.g.*, Chinner *et al.*, 1969; Fyfe and Mackenzie, 1969; Pitcher, 1965). In this study, eight andalusites and sillimanites, including two coexisting pairs of the minerals, were carefully purified and analyzed for major and minor chemical constituents.

Occurrence of the Alumino-Silicates

Andalusite. Since Blake (1858) first noted the occurrence of andalusite in rocks of the Sierra Nevada, innumerable workers have reported its presence. It is the common Al₂SiO₅ polymorph in metamorphosed pelitic and quartzo-feldspathic metasedimentary rocks of the region, has been found as a rare constituent in some pegmatites (MacDonald and Merriam, 1938; Rose, 1957), and in one instance has been reported in altered metavolcanic rock (Huber and Rinehart, 1965). The mineral occurs either in

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sieved, sponge-like anhedra or in well-formed, prismatic euhedra, often up to a few centimeters long. The chiastolite variety of andalusite occurs both in contact zones in the metamorphic belt along the western margin of the Sierra Nevada baholith and in some of the larger roof pendants associated with the batholith. Andalusite, and particularly the chiastolite variety, is commonly replaced in varying amounts by fine-grained sericite.

Sillimanite. Although not nearly as common as andalusite, sillimanite has been noted in metamorphosed pelitic rocks of the Sierra Nevada and Inyo Mountains by several workers (Bateman, 1965; Best and Weiss, 1964; Clarke, 1915; Durrell, 1940; Fairbanks, 1890; Kerrick, 1970; Knopf, 1917; Miller, 1931; Moore, 1963; Rose, 1957; Ross, 1969; Turner, 1896). The mineral generally occurs either in fine-grained, rope-like aggregates of fibrolite or in single, relatively large, prismatic crystals disseminated through the host rock. In a number of the reported occurrences, sillimanite accompanies andalusite. There usually is no particular mutual relationship between the two minerals although in some occurrences sponge-like parts of grains of andalusite grade into fine, acicular masses of sillimanite, suggesting replacement of one of the polymorphs by the other. Some of the larger, prismatic crystals of sillimanite are partly altered to sericite; fibrolite bundles are generally unaltered.

One of the purposes of this study was to verify the presence of sillimanite and the absence of mullite, because distinction of sillimanite from mullite is difficult. Mullite was searched for but not found in rocks from localities where sillimanite had been previously identified (sillimanite was distinguished by density determinations augmented with semiquantitative spectrographic and X-ray diffraction methods). In addition, Moore and Best (1969) have positively shown by careful measurement of the unit cell that fine, acicular, fibrous material from hornfels of the southern Sierra Nevada is sillimanite. On the basis of these studies, it is extremely unlikely that mullite occurs in rocks of the Sierra Nevada and Inyo Mountains.

Kyanite. Kyanite has been reported at one locality in the Sierra Nevada by Sampson and Tucker (1931, p. 457), who noted that it is "A constituent of the schists on Yankee Hill" but provided no further details. Yankee Hill is approximately 4 km east of the town and California state historical monument of Columbia in the western metamorphic belt of the Sierra Nevada. Several rock samples were collected there and carefully examined to confirm the reported kyanite occurrence; however, the mineral was not identified in any of the samples. The failure to confirm

the mineral occurrence, and the lack of details in Sampson and Tucker's report cast doubt on the validity of this occurrence.

Although kyanite was not found in bedrock from Yankee Hill, and has not been reported in metamorphic rocks elsewhere in the Sierra Nevada, the mineral was recognized as a detrital constituent of stream sediment collected near Yankee Hill. Approximately 1 kg of sediment was taken at the base of the hill from a stream bank just below the convergence of two ephemeral streams that drain the hill (lat. 38°02′18″N., long. 120°00′12″), and after exhaustive treatment to concentrate kyanite, three grains of the mineral were optically identified. The source of the mineral is unknown, although it may be related to the enigmatic source of detrital diamonds, which have also been discovered in various placer deposits of the Sierra Nevada (Murdoch and Webb, 1966). Bedrock at levels now exposed in the Sierra Nevada has probably never been exposed to physical conditions suitable for the formation of kyanite. The detrital kyanite may have been brought to the surface, from deep crustal levels, in xenoliths in volcanic rocks. High-pressure xenolith assemblages have recently been discovered in the central Sierra Nevada foothills south of the kyanite detritus is greatly complicated by the presence of Tertiary river gravels upstream from the sample locality.

Compositions of Andalusites and Sillimanites

Andalusites and sillimanites selected for analysis were purified by centrifuging washed rock powders (minus 250 or 325 mesh) in carefully adjusted mixtures of heavy liquids and by repeated electromagnetic fractionation. Impurities generally made up less than one percent of the analyzed separates. Optical inspection of the separates indicated that contamination was restricted to small inclusions of apatite, zircon, graphite, hematite, and other extremely fine, unidentified phases. Electron microprobe scans for Cr, V, and K across several grains from the different separates showed no significant concentrations of these elements, indicating that their distribution is not related to submicroscopic impurities. Materials were analyzed by standard gravimetric techniques or by a combination of atomic absorption, spectrometric, flame photometric, and colorimetric methods and by emission spectrography (Tables 1 and 2). Several elements were below the detectibility level of the spectrographic method.

Analyses were recalculated assuming 20 oxygen atoms per unit cell (that is, four formula units per unit cell), using a computer program designed by Jackson *et al.*, (1967). As is common, analyzed andalusites and sillimanites are nearly pure Al_2SiO_5 (*e.g.*, Deer *et al.*, 1962). The Al:Si atomic ratio of all the analyzed minerals is slightly less than the

TABLE 1. COMPOSITIONS OF ANDALUSITES

	V-7-S	FD-21	E-99	B-281
Chemical analyses (weight percent)[a]				
SiO_2	37.44	36.96	37.18	37.0
Al_2O_3	61.46	61.59	61.19	60.2
Fe_2O_3	.62	.64	.77	1.32
MgO	.06	.16	.06	.11
CaO	.17	.21	.22	.33
Na_2O	0	0	0	0
K_2O	.02	.04	.06	.12
H_2O	0	.06	.06	.40
TiO_2	.10	.08	.12	.03
P_2O_5	.02	.03	.05	.08
Total	99.87	99.77	99.82	99.6

Spectrographic analyses (weight percent)[b]				
B	<.002	<.002	<.002	<.002
Ba	<.0002	.0018	<.0002	.024
Cr	.027	.010	.080	.035
Cu	.0012	.0022	.0018	.0040
Ga	.0070	.0050	.0090	.0044
La	<.004	<.004	<.004	<.004
Mn	.0007	.0022	.0004	.0050
Ni	<.0002	<.0002	.0004	.0005
Sc	<.0004	<.0004	<.0004	<.0004
Sr	<.0002	<.0002	<.0002	.0009
V	.014	.013	.025	.014
Y	<.002	<.002	<.002	<.002
Yb	<.0002	<.0002	<.0002	<.0002
Zr	<.001	<.001	.012	.011

Number of ions on basis of 20 (O)				
Si	4.053	4.015	4.040	4.054
B	0	0	0	0
Al	7.842	7.884	7.836	7.774
Ga	.001	.001	.001	0
Cr	.003	.001	.010	.004
Fe	.051	.052	.063	.109
Ti	.008	.007	.010	.003
V	.002	.002	.003	.002
Mg	.010	.026	.010	.018
Ca	.020	.020	.018	.026
K	.003	.006	.008	.017
	} 7.94	} 8.00	} 7.96	} 7.95

Sample locations and descriptions given in appendix.

[a] Chemical analyses of V-7-S, FD-21 and E-99 by C. O. Ingamells and analysis of B-281 by H. N. Eisheimer and Marcelyn Cremer.

[b] Spectrographic analyses by R. E. Mays.

TABLE 2. COMPOSITIONS OF SILLIMANITES

	V-7-S	E-77	W-261A	B-281
Chemical analyses (weight percent)[a]				
SiO_2	36.5	37.4	37.8	—
Al_2O_3	61.4	61.2	61.2	—
Fe_2O_3	.67	.57	.51	—
MgO	.08	.07	.06	—
CaO	.62	.34	.25	—
Na_2O	0	0	0	—
K_2O	0	0	0	
H_2O	.72	.10	.09	—
TiO_2	.04	.03	.03	—
P_2O_5	.28	.16	.08	—
Total	100.3	99.8	100.1	
Spectrographic analyses (weight percent)[b]				
B	.036	.014	.026	.030
Ba	<.0002	<.0002	<.0002	.014
Cr	.060	.11	.11	.11
Cu	.0018	.0018	.0055	.0036
Ga	.011	.0085	.0075	.0075
La	.008	<.004	<.004	<.004
Mn	.0016	.0026	.0004	.0065
Ni	<.0002	<.0002	.0004	.0024
Sc	.0010	.0018	.0018	.0033
Sr	<.0002	<.0002	<.0002	.0004
V	.045	.12	.10	.11
Y	.005	<.002	<.002	<.002
Yb	.0005	<.0002	<.0002	<.0002
Zr	.032	.009	.004	.18
Number of ions on basis of 20 (O)				
Si	3.980	4.055	4.081	—
B	.023	.008	.016	—
Al	7.891	7.821	7.787	—
Ga	.001	.001	.001	—
Cr	.008 8.04	.014 7.94	.014 7.90	—
Fe	.055	.047	.041	—
Ti	.003	.002	.002	—
V	.006	.016	.013	—
Mg	.013	.011	.010	—
Ca	.044	.015	.016	—
K	0	0	0	

Sample locations and descriptions given in appendix.

[a] Chemical analyses by H. N. Elsheimer and Marcelyn Cremer.

[b] Spectrographic analyses by R. E. Mays.

stoichiometric ratio of 2.0, suggesting substitution for minor amounts of Al by trace elements, and in some cases, by Si.

Detected elements present in minor amounts preferentially concentrated in one of the two alumino-silicate minerals include B, Cr, Sc, and V in sillimanite and K in andalusite. Other elements show vague or no appreciable preference for either phase. Somewhat similar elemental distributions have been noted by Pearson and Shaw (1960) for materials from throughout the world. The bulk of the P and Zr most likely represents trace amounts of contaminants; however, contents of other elements, with the possible exception of Ca, are not appreciably influenced by impurities in the analyzed separates. In view of the crystal-chemistry of the alumino-silicates, the preferential concentration of individual elements between the two alumino-silicate phases is not particularly surprising. Boron apparently proxies for tetrahedrally coordinated Al, and Cr, Sc, and V substitute for octahedrally coordinated Al in sillimanite. The site occupied by Al in andalusite is a five-coordinated, trigonal pyramidal one and is less conducive to substitution by B, Cr, Sc, and V. Potassium, on the other hand, preferentially enters andalusite because of the more open nature of the mineral's lattice, and the element probably simply occupies void space—a similar explanation for presence of large alkali atoms in alumino-silicates in general has been proposed by Pearson and Shaw (1960).

In addition to the compositional data presented in this paper, Okrush and Evans (1970) have recently published microprobe analyses of a coexisting andalusite and sillimanite pair from the May Lake area of the Sierra Nevada. In contrast to the results of this study, Okrush and Evans reported K less than 0.01 percent and no differences in Cr and V contents of the two phases.

CONCLUSIONS

The barometric significance of Al_2SiO_5 polymorphs in rocks of the Sierra Nevada has been discussed by Bateman and Eaton (1967) and Evernden and Kistler (1970). These authors note that the regional occurrence of andalusite and the complete exclusion of kyanite in the metamorphic rocks indicate that the maximum total pressure that the rocks have been subjected to was at or below the upper pressure limit of andalusite stability. This in turn defines the maximum possible total pressure during emplacement of the associated Sierra Nevada batholith. In known Sierran occurrences, sillimanite has developed as a result of contact metamorphism rather than regional metamorphism, and thus is important as an indicator of temperature, but not necessarily pressure. It is interesting to note that the reported sillimanite occurrences are gen-

erally associated with the older granitic rocks of the batholith, which predate the Late Cretaceous. The sillimanite-bearing rocks from near Isabella (Best and Weiss, 1964) in the southern Sierra Nevada may be an exception; however, recent unpublished field studies by R. W. Kistler and the author indicate that the May Lake sillimanite occurrence reported by Rose (1957) is associated with granitic rocks older than originally thought. This suggests that as a rule the older plutonic rocks were emplaced at either greater pressures or higher temperatures than were their younger counterparts. It seems more likely that the older rocks were emplaced at slightly deeper levels than the younger rocks; thus a small pressure effect, rather than a temperature effect, was responsible for production of sillimanite.

As noted, the two alumino-silicate polymorphs found in rocks of the Sierra Nevada and Inyo Mountains are not strictly isochemical, but rather there is a consistent and distinct distribution pattern of trace elements between the two phases. Free energy and entropy differences of the andalusite-sillimanite reaction are small, and it is possible that trace element partitioning may greatly alter stability relationships. In spite of the numerous recent papers published on the Al_2SiO_5 system, at present little can be said about the precise effect of selective trace-element distribution on stability fields of the individual polymorphs. Albee and Chodos (1969) argued that solid solution of minor elements, particularly Fe, was not sufficient to account for the coexistence of different Al_2SiO_5 phases in rocks studied from two different areas. Chinner *et al.*, (1969) and Okrush and Evans (1970) advanced similar conclusions for coexisting minerals they examined. Nevertheless, the presence of sillimanites and andalusites of differing trace-element contents suggests the possibility that foreign ion stabilization, rather than or in addition to simple metastable persistence, may have played a role in survival of the polymorphs in rocks of the Sierra Nevada and Inyo Mountains.

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APPENDIX

SAMPLE DESCRIPTIONS, LOCATIONS, AND COLLECTORS

V-7-S: Spongy andalusite and fine, fibrous sillimanite in pelitic hornfels. Collected from

the Triassic(?) Three Rivers Schist of Durrell (1940), northwest quarter of the Kaweah U. S. Geol. Surv. 15′ quadrangle, by P. C. Bateman.

FD-12: Coarse, porphyroblasts of andalusite (chiastolite) in graphitic slate. Collected from the Jurassic Mariposa(?) Formation, northwest quarter of the Raymond U. S. Geol. Surv. 15′ quadrangle, by F. C. W. Dodge.

E-99: Subhedral andalusite in pelitic hornfels. Collected from the Cambrian Harkless Formation, northwest corner Waucoba Wash U. S. Geol. Surv. 15′ quadrangle, by E. M. MacKevett.

B-281: Spongy andalusite and fine, fibrous sillimanite in pelitic hornfels. Collected from a small, unnamed roof remnant, northwest quarter of the Mount Pinchot U. S. Geol. Surv. 15′ quadrangle, by J. G. Moore.

E-77: Coarse, prismatic sillimanite in pelitic hornfels. Collected from the Devonian Lost Burro(?) Formation, southwest quarter of the Waucoba Wash U. S. Geol Surv. 15′ quadrangle, by E. M. MacKevett.

W-261A: Subhedral sillimanite in pelitic hornfels. Collected from undivided Paleozoic rocks, southwest quarter of the Waucoba Wash U. S. Geol. Surv. 15′ quadrangle, by D. C. Ross.