Chloritoid-sillimanite assemblage from North Carolina

DANIEL J. MILTON

U.S. Geological Survey, 928 National Center, Reston, Virginia 22092

ABSTRACT

Chloritoid and sillimanite in apparent equilibrium occur in a quartzite near Charlotte, North Carolina. The chloritoid is Fe-rich [Fe/(Fe + Mg) = 0.96 to 0.99], as is that from two occurrences in New Mexico from which this assemblage has been reported. The existence of a chloritoid-sillimanite stability field is predicted from experimental studies on the reaction of Fe-rich chloritoid with aluminum silicate if the kyanite-andalusite-sillimanite triple point lies at a temperature near 500°C, but is incompatible with a higher-temperature triple point.

INTRODUCTION

The kyanite-andalusite-sillimanite (KAS) triple point is a key benchmark in constructing the petrogenetic grid for metamorphic rocks, but its determination is experimentally difficult and its P-T coordinates are still in dispute. Valuable information is provided by natural associations of the aluminum silicate minerals with other minerals whose reactions are more amenable to experimental study. It is thus an important question whether the reasonably well known equilibrium curve (Richardson, 1968; Rao and Johannes, 1979)

$$\text{chloritoid} + \text{Al silicate} = \text{staurolite} + \text{quartz} + \text{water} \quad (1)$$

passes to the high- or low-temperature side of the KAS triple point. Chloritoid-sillimanite assemblages have been described from the Picuris Range, New Mexico, by Holdaway (1978) and from the Truchas Peaks, New Mexico, by Grambling (1981, 1983) (occurrences 35 km apart, but perhaps in a single terrane displaced by postmetamorphic faulting). These authors consider the assemblage evidence for a low-temperature KAS triple point, such as that proposed by Holdaway (1971), within the chloritoid stability field. In contrast, Bickle and Archibald (1984), acknowledging but not explaining the New Mexico occurrences, feel that the extreme rarity of the chloritoid-sillimanite assemblage favors a high-temperature triple point, such as that proposed by Richardson et al. (1969), outside the stability field of chloritoid.

OCCURRENCE

A sillimanite-chloritoid assemblage was found in the Charlotte belt of the North Carolina Piedmont, on a small knob just southwest of the confluence of Torrence and MacDowell Creeks, about 20 km north of Charlotte, North Carolina (Lake Norman South 7½′ quadrangle). Two samples were collected, a quartzite with sillimanite and magnetite, and the subject of this note, a quartzite consisting of quartz, sillimanite, chloritoid, muscovite, pyrite, and rutile. Numerous small bodies of high-alumina quartzite

occur in the Charlotte belt near Charlotte. Their occurrence as irregular nonstratiform bodies associated with metavolcanic rocks, and their composition, with the usual presence of rutile and occasional presence of pyrite, gahnite, and aluminum phosphate minerals (lazulite, rarely trolleite and augelite) suggest that the protoliths were hydrothermally altered volcanic material rather than sedimentary rocks. A scapolite-bearing epidote amphibolite collected about 100 m to the west may have had a less-altered volcanic protolith. Metamorphism is of the regional type; from reconnaissance field work, the conditions cannot be specified more closely than being close to the KAS triple point. Sillimanite occurs without chloritoid in other rocks in the vicinity, kyanite-chloritoid-quartz-muscovite rock and a quartzite with fibrolitic sillimanite and rare grains of chloritoid were collected about 15 km to the north, and an andalusite-quartz-muscovite rock was collected a similar distance to the south.

PETROGRAPHY

The specimen studied consists of 60% quartz, 20% muscovite, 15% sillimanite, 2% chloritoid, 2% pyrite, and a trace of rutile. Muscovite tends to occupy the interstices between quartz grains, with crystals showing a continuum of sizes from coarse grains to fine sericitic aggregates. All the muscovite is sodic, but there is a rough inverse relation between grain size and Na content; the larger grains have compositions clustering about $Mu_{73}Pa_{27}$, and the sericitic aggregates have a wide range of compositions with individual spots analyzed with the microprobe being as sodic as $Mu_{40}Pa_{60}$. The latter composition is well within the muscovite-paragonite solvus, suggesting an unresolved intergrowth of phases on a scale of <1 μm. Sillimanite forms prisms as large as 0.3×0.7 mm, never fibrolitic needles. Chloritoid forms subhedral equant grains up to 2 mm across, commonly but not always intergrown with sillimanite prisms. Chloritoid is monoclinic, as indicated by the powder-diffraction pattern, and polysynthetically twinned. Pyrite forms subhedral cubes up to 2 mm across.

There is no textural evidence of disequilibrium between

Table 1. Microprobe analyses of chloritoid

	Grain 1			Grain 2		
	average (28 points)	high Mg + Mn point	low Mg + Mn point	average (42 points)	high Mg + Mn point	low Mg + Mn point
			Weight percent oxide			
FeO	27.25	26.87	27.61	27.36	27.04	27.98
MgO	.41	.54	.20	.49	.65	.23
MnO	.44	.51	.30	.50	.55	.36
Al_2O_3	40.73	40.79	40.64	41.29	41.06	41.59
SiO_2	23.73	23.74	23.20	23.62	23.67	23.47
H_2O*	7.18	7.19	7.16	7.17	7.18	7.16
Total**	99.74	99.64	99.11	100.43	100.14	100.79
			Cations based on 12 oxygens			
Fe	1.907	1.880	1.952	1.902	1.882	1.948
Mg	.051	.068	.025	.061	.081	.028
Mn	.031	.036	.021	.035	.039	.025
Al	4.019	4.022	4.049	4.045	4.029	4.068
Si	1.987	1.986	1.961	1.963	1.970	1.948
Total	7.995	7.992	8.008	8.006	8.001	8.011
Fe/Fe+Mg	.973	.965	.987	.969	.959	.986
Fe/Fe+Mg+Mn	.959	.948	.979	.952	.940	.973

*H_2O calculated for assumed 4(OH) per formula unit.

**Oxides not found (and detection limits, weight percent): ZnO (0.07), CaO, TiO_2, Na_2O (0.02).

any of the phases. The muscovite appears to be prograde. The only replacement relationships apparent are the growth of sillimanite and chloritoid in quartz and in muscovitic aggregates and the growth of sillimanite prisms across apparently earlier-formed chloritoid (Fig. 1).
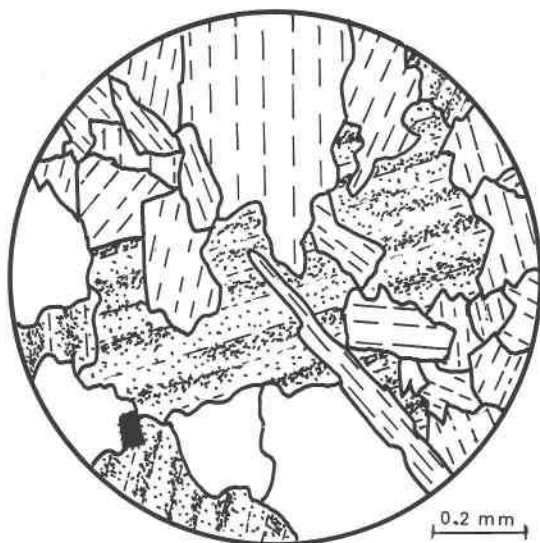

Fig. 1. Chloritoid (polysynthetically twinned), sillimanite (cleaved), quartz, and small grain of rutile (dark) in quartzite, McDowell Creek, North Carolina.

CHLORITOID COMPOSITION

A number of chloritoid grains were analyzed. The most satisfactory analyses were obtained from two typical grains (Table 1) with an automated ARL SEMQ 9-channel microprobe, at 20 kV and 0.1-μA beam current, using natural and synthetic standards, correction for background counts proportional to the average atomic number of the standards and unknowns, and Bence-Albee–type matrix-correction procedures. Replicate analyses of single points yielded the following standard deviations: SiO_2, 0.3 wt%; Al_2O_3 and FeO, 0.1 wt%; MgO, and MnO, 0.02 wt%; these values are close to those that would be predicted simply on the basis of counting statistics. Analyses of the chloritoid with different analytical programs or different standardization suggest that the accuracy may be lower than the precision. Specifically, there is no reason to believe the deviations from stoichiometry in Table 1 reflect reality.

The chloritoid is Fe rich; its composition varies within fairly narrow limits. There is a strong correlation of Mg and Mn contents, as may be seen on the triangular plot (Fig. 2). The correlation is not linear; the Mg/Mn ratio increases with the content of these components. A zoning pattern, with higher Mg and Mn in the outer zone, is commonly shown by grains traversed parallel to the cleavage (a somewhat asymmetrical example is shown in Fig. 3), whereas grains traversed across the cleavage usually show no regular pattern. There would seem to be no crys-
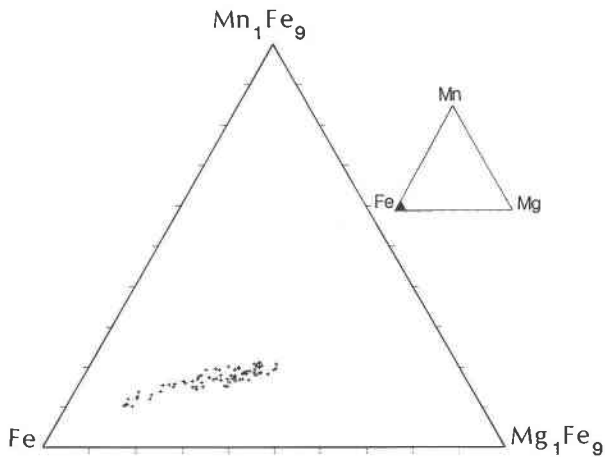
Fig. 2. Plot of atomic ratios of Fe, Mg, and Mn in chloritoid. Area corresponds to shaded corner of inset triangle.

Fig. 3. Compositional profiles across a chloritoid grain, parallel to the cleavage. Analyzed points are 15 μm apart, on two parallel traverses also 15 μm apart.

tallochemical reason for the covariance of Mg and Mn; it presumably reflects fluctuations in the environment of formation of the chloritoid. Both elements may have been contained in one predecessor phase (perhaps a chlorite), which supplied Mg and Mn in constant or slowly changing proportions as it decomposed during prograde metamorphism.

PETROLOGY

Sillimanite and chloritoid are not uncommonly found in association, but as disequilibrium assemblages. In the eastern North Carolina Piedmont, for example, sillimanite relict from a Proterozoic metamorphism is partially replaced by chloritoid produced during a late Paleozoic metamorphism (Farrar, 1985). Sillimanite and chloritoid in equilibrium are indeed rare; this and the Truchas-Picuris occurrences are apparently the only ones recorded. An old report (Papavasiliou, 1913), still occasionally cited, of sillimanite in chloritoid emery from Naxos is apparently in error (Feenstra, 1985, p. 66).

Chloritoid would break down at a lower temperature in an environment with $P_{H_2O} < P_{tot}$ than in one with $P_{H_2O} = P_{tot}$. The first situation may obtain more generally in pelitic rocks than in quartzites, but probably not so universally as to preclude the equilibrium of chloritoid and sillimanite. Higher f_{O_2} displaces Reaction 1 to higher temperatures (Ganguly, 1972), favoring the chloritoid-sillimanite assemblage, but this is probably not a significant factor in the North Carolina occurrence. Fe^{3+} was not determined in the chloritoid, but its content must be small, especially as there is no apparent deficiency in Al. Pyrite, the only other Fe-bearing phase, would be stable at a wide range of redox conditions, but the presence of magnetite rather than hematite in other rocks from the outcrop, however, suggests that f_{O_2} was no higher than the hematite-magnetite buffer.

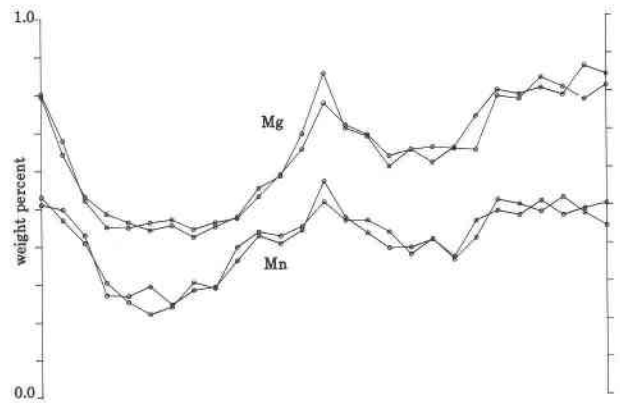The critical factor allowing the assemblage would appear to be a high Fe/Mg ratio in the chloritoid and in the rock as a whole. Like the McDowell Creek chloritoid, 11 out of 12 of Grambling's (1983) chloritoids coexisting with sillimanite fall between $X_{Fe} = 0.95$ and 1.00 (with one at $X_{Fe} = 0.88$ still to be explained). The experimental determinations of Reaction 1 have been for the Fe endmember system, which, in the ideal simple system would be the low-temperature limit of a family of curves for the breakdown of chloritoids of increasing Mg content. However, in the New Mexico occurrences, Grambling (1983) found a reversal of Fe-Mg partitioning between chloritoid (ctd) and staurolite (stt) whereby $X_{Fe}^{ctd} > X_{Fe}^{stt}$ above about $X_{Fe} = 0.91$ and $X_{Fe}^{ctd} < X_{Fe}^{sst}$ below $X_{Fe} = 0.91$. Of several possible causes, the one he favors, nonideal mixing of Mg and Fe in one or both minerals, implies a minimum temperature for Reaction 1 at the reversal composition. It may be only unusually low Mg rocks that approximate the experimental systems so far investigated. The compositions of common pelitic rocks favor chloritoid and staurolite compositions nearer the critical composition, which may shift Reaction 1 to temperatures sufficiently low that the chloritoid-sillimanite stability field is suppressed.

The various experimental determinations of Reaction 1 in Fe endmember systems, however, fit the occurrence reported here from McDowell Creek and those at the Truchas Peaks and the Picuris Range. These experiments, together with the natural assemblages, indicate a temperature for the KAS triple point in the vicinity of 500°C, supporting the Holdaway (1971) rather than the Richardson et al. (1969) placement.

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