Chapter 3

The Sillimanite Minerals: Andalusite, Kyanite, and Sillimanite

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Abstract The chemistry and the mineralogy of the three Al$_2$O$_3$·SiO$_2$ sillimanite minerals (andalusite, kyanite, and sillimanite) are described. Their $P$–$T$ diagram is discussed. The structural differences among the three are reviewed, emphasizing the coordination of the Al$^{3+}$ cations that link the double octahedral chains within the structures. Their decompositions to produce mullite and silica are described and contrasted. The effect of nanomilling on those decompositions is discussed. Finally, the locations of commercial deposits and the industrial applications are addressed.

1 Introduction

The sillimanite minerals are the three anhydrous aluminosilicates: andalusite, kyanite, and sillimanite [1,2]. Kyanite is also referred to as cyanita, cyanite, and disthene. Because all three have the same 1:1 molar ratio of alumina (Al$_2$O$_3$) to silica (SiO$_2$), they are often written simply as Al$_2$O$_3$·SiO$_2$ or Al$_2$SiO$_5$. Their ideal composition is 62.92 wt% alumina and 37.08 wt% silica. However, in natural states involving significant impurities, the alumina content is usually less than 60 wt%. There are reports of higher alumina content deposits associated with the presence of higher alumina content minerals. That such a mineral group exists is not surprising, for the three most common elements in the Earth’s crust are O, Si, and Al.

The three sillimanite minerals are not found in phase diagram of the familiar binary alumina–silica at a pressure of 1 atm. This phase diagram has only the single aluminosilicate compound known as mullite, 3Al$_2$O$_3$·2SiO$_2$ (71.79 wt% alumina and 28.21 wt% silica) [3–5]. The absence of the three sillimanite minerals on the binary diagram is because they are geologically formed at high pressures and elevated temperatures within the earth. None of the three minerals of the sillimanite group are equilibrium phases at 1 atm pressure. However, the three do exist in their metastable states throughout the world, quite abundantly in many geologically favorable areas. They are often discussed simultaneously with mullite, for their chemistries and crystalline structures are related to that of mullite. Furthermore, the three sillimanite polymorphs form mullite by decomposition when heated to elevated temperatures. This characteristic is the basis of their industrial utility.
The $P-T$ diagram of the three sillimanite minerals is presented in Fig. 1. This $P-T$ diagram for the Al$_2$SiO$_5$ compound is somewhat controversial to the precise $P-T$ values for the equilibrium triple point of the three polymorphs. Four sets of triple point $P-T$ data, three experimental and one theoretical, are listed in this diagram. It is evident that the triple point is located at approximately 3–6 kbar pressure and a temperature of approximately 400–650°C. Kyanite is the high-pressure structure of the three, while sillimanite is the high-temperature structure. Andalusite occurs at lower pressures and temperatures. When the three minerals are heated above approximately 1,200°C in air, they will decompose to produce the stable compound mullite and reject very fine, highly reactive silica. The decomposition temperatures vary for the three sillimanite minerals as does the structural form of the rejected silica. The decompositions will be discussed further below.

It is important to address a few issues regarding the three polymorph densities as they appear in the $P-T$ diagram of Fig. 1. Generally, high temperature polymorphs of materials are less dense than low temperature ones. However, this is not the case when andalusite ($-3.1 < \rho < -3.2$ Mg m$^{-3}$) is compared with sillimanite ($-3.2 < \rho < -3.3$ Mg m$^{-3}$). In this comparison, the high temperature form, sillimanite, is denser. This apparent anomaly occurs because of a change in the coordination number of a portion of the Al cations within the crystal structure. The coordination change is from the unusual value of fivefold within andalusite to just fourfold within sillimanite. The density effects of pressure are to be expected with the high-pressure polymorph, kyanite, having the highest density ($-3.5 < \rho < -3.7$ Mg m$^{-3}$).

A number of properties [6] of the sillimanite group minerals and those of mullite as well are summarized in Table 1. These properties merit brief discussion. The three minerals have relatively large unit cells and complex crystal structures. Their crystal habits reflect their easy and well-defined cleavage planes. They are not very hard minerals by any measure, typically in the middle of the Mohs hardness scale. Perhaps