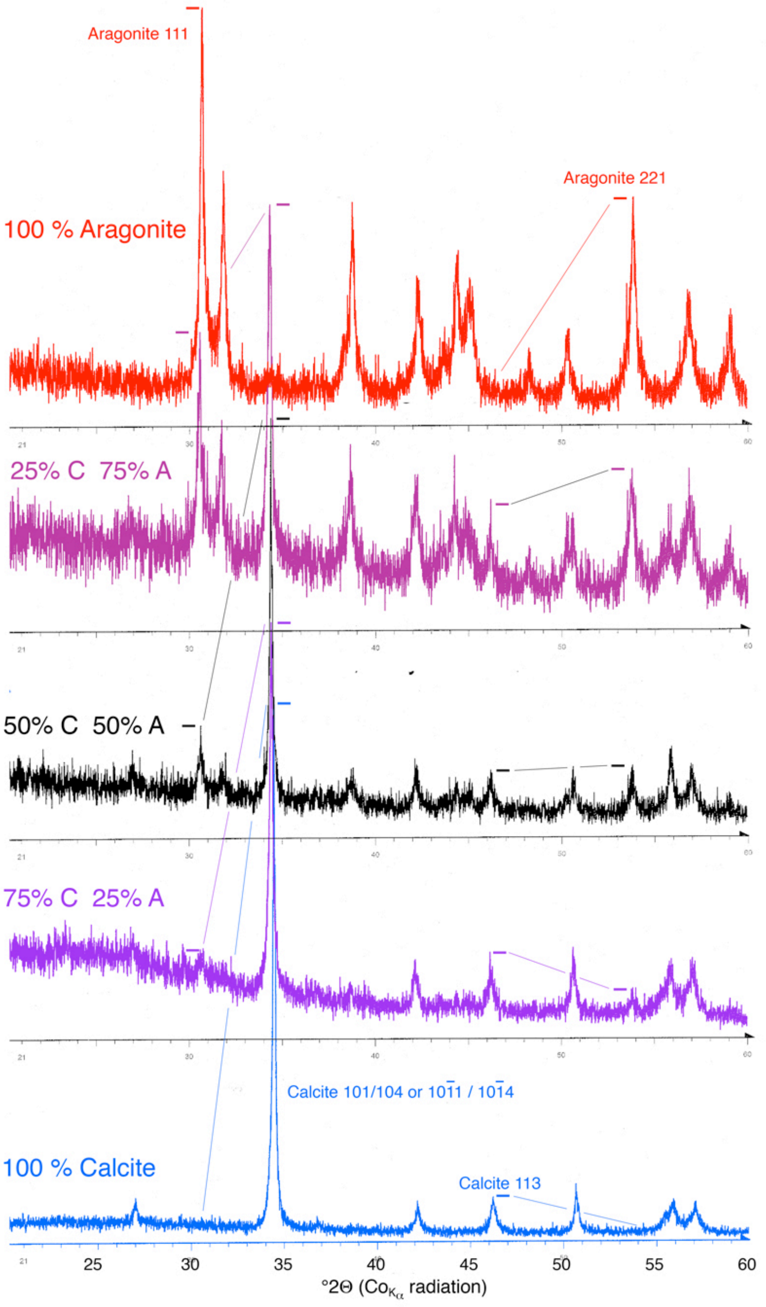
X-ray diffraction (XRD) of aragonite and calcite



X-ray diffraction provides an easy way to distinguish between the two polymorphs of $CaCO_3$, aragonite and calcite. The two minerals have their highest-intensity peaks at different positions, and the general look of the two patterns is different. Aragonite has its greatest peak (111) at relatively small °2Θ and has several lesser peaks, whereas calcite has a booming 104 peak a bit to the right of the aragonite large peak, and few and comparatively small other peaks.

That difference in patterns, if convenient for quick identification of a pure sample, makes analysis of mixtures a bit more challenging. The calcite 104 peak is so robust that it is typically larger than the aragonite 111 peak, even in a mixture that is 75% aragonite. The aragonite peak, in contrast, begins to disappear in the noise of a calcite XRD pattern if aragonite is less than 25% of the sample. Thus comparison of the most intense peaks becomes a tricky and potentially misleading enterprise.

The usual solution to this problem is to use the aragonite 221 peak as an indicator of the abundance of aragonite. For example, Dickinson and McGrath (2001, *The Analyst* 126, 1118–1121) used the ratio of integrated peak areas (not heights) of the calcite 104 and aragonite 221 peaks to develop a quantitative relationship for ratio of aragonite to calcite. That approach yields good quantitative results, if with the somewhat unsettling proviso that a 50-50 mixture of the two ploymorphs has a 104/221 intensity ratio much greater than 1, because of the exceptional intensity of the calcite 104 peak.

Another approach that yields a more intuitively acceptable result is to compare the calcite 113 and aragonite 221 peaks. In this case, an 50-50 equal mixture of calcite and aragonite generates peaks of about the same height, facilitating a quick-look approach. On a pattern generated with $Co_{K\alpha}$ radiation, these peaks are at about 46 and 54 °2Θ, and thus conveniently symmetrically positioned around 50°. On a pattern generated with $Cu_{K\alpha}$ radiation, they're at about 40 and 46 °2Θ, not quite so conveniently symmetrically positioned around 43°, but not hard to find.