

$\Delta 2\theta_{131-1\bar{3}1}$ for albites crystallized in the systems
 $\text{NaAlSi}_3\text{O}_8\text{-}\beta\text{-LiAlSi}_2\text{O}_6\text{-H}_2\text{O}$ and
 $\text{NaAlSi}_3\text{O}_8\text{-LiAlSiO}_4\text{-H}_2\text{O}$

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Summary. Values of $\Delta 2\theta_{131-1\bar{3}1}(\text{Cu-K}\alpha)$ have been determined for albites crystallized in the system $\text{NaAlSi}_3\text{O}_8\text{-}\beta\text{-LiAlSi}_2\text{O}_6\text{-H}_2\text{O}$ at various pressures, temperatures, and times. These values are consistently higher than those reported by MacKenzie (1957) for pure synthetic albites crystallized under similar conditions. Data of the present study have been combined with that of Stewart (1960) for albites crystallized in the system $\text{NaAlSi}_3\text{O}_8\text{-LiAlSiO}_4\text{-H}_2\text{O}$ and, when plotted against bulk Li_2O content, show constant $\Delta 2\theta_{131-1\bar{3}1}$ values at approximately 1.0 wt. % Li_2O . The addition of Li to albites has a much more pronounced effect on the $\Delta 2\theta_{131-1\bar{3}1}$ parameter than the addition of K or Ca. Albites from lithium-rich pegmatites have much lower $\Delta 2\theta_{131-1\bar{3}1}$ values and are similar to those of synthetic low albites. The differences in this parameter between the natural and synthetic specimens are believed to be caused by differences in the structures of the coexisting lithium minerals in the natural and synthetic environments.

DURING an investigation of phase relations in the system $\text{NaAlSi}_3\text{O}_8\text{-}\beta\text{-LiAlSi}_2\text{O}_6$ at 2 Kb $P_{\text{H}_2\text{O}}$, consistently higher values of $\Delta 2\theta_{131-1\bar{3}1}$ were obtained for albites crystallized in the presence of lithium compared to those recorded for pure synthetic albites by MacKenzie (1957). Similar high values of this parameter were reported by Stewart (1960) for albites crystallized in the system $\text{NaAlSi}_3\text{O}_8\text{-LiAlSiO}_4$ at the same $P_{\text{H}_2\text{O}}$. In the present study, the $\Delta 2\theta_{131-1\bar{3}1}$ values for albites crystallized in the present system have been combined with the values reported by Stewart (1960) and MacKenzie (1957) and this parameter plotted against bulk Li_2O content. Experiments were done in conventional cold-seal pressure vessels (Tuttle, 1949) using sealed-tube techniques (Goranson, 1931) and coprecipitated gels, made by a modification of the method described by Roy (1956), as starting materials.

Data of our experiments and the pertinent data from Stewart (1960) and MacKenzie (1957) are shown in table I. In fig. 1, $\Delta 2\theta_{131-1\bar{3}1}$ has been

plotted against bulk Li_2O content for runs at 2 Kb (approx.) and for various temperatures and times. Slight discrepancies between the values of the present study and those of Stewart and MacKenzie may be due to small differences in temperatures, lengths of crystallization, and

TABLE I. $\Delta 2\theta_{131-1\bar{3}1}$ (Cu- $K\alpha$) for albites crystallized in the systems $\text{NaAlSi}_3\text{O}_8$ - β - $\text{LiAlSi}_2\text{O}_6$ - H_2O and $\text{NaAlSi}_3\text{O}_8$ - LiAlSiO_4 - H_2O (Stewart, 1960). All data for 2000 bars $P_{\text{H}_2\text{O}}$ except where indicated. Li_2O is wt. % in bulk

Temp. ° C	Time	Li_2O %	$\Delta 2\theta_{131-1\bar{3}1}$	Most closely corresponding value for pure albite (MacKenzie, 1957)
700*	160 hr	0.0	1.864†	—
700*	800	0.0	1.806†	—
720-50†	72-108	0.0	1.905†	—
600‡	150	0.4	1.902	1.832, 1.840
700‡	792	0.4	1.877	1.806¶
825‡	358	0.4	1.952	1.935‡
700	160	0.4	1.922	1.864¶
750	108	0.4	1.924	1.911‡
700	160	0.8	1.923	1.864¶
730	72	0.8	1.963	1.908‡
745	74	0.8	1.947	1.914‡
700**	800	1.2	1.893	1.806¶
720-50**	72-108	1.2	1.983	—
720-50**	72-108	1.8	1.992	—
700**	800	2.4	1.893	1.806¶
700**	160	2.4	1.930	1.864¶
720-50**	72-108	2.4	2.020	—
700**	160	6.0	1.925	1.864¶

* 28 000 lb/in.² $P_{\text{H}_2\text{O}}$.

† 14 000 lb/in.² $P_{\text{H}_2\text{O}}$.

‡ MacKenzie (1957, graph, p. 493).

§ 1000 bars $P_{\text{H}_2\text{O}}$.

|| MacKenzie (1957, p. 490).

¶ MacKenzie (1957, p. 491).

** Stewart (1960).

starting materials. The presence of a coexisting lithium mineral (β -spodumene)¹ in all runs of the present study, and α -eucryptite in Stewart's runs, indicates that the weight % Li_2O , plotted on fig. 1, does not reflect the lithium content in the albite, but simply the Li_2O content in the bulk compositions.

The most pronounced feature of the curves in fig. 1 is the constant value of $\Delta 2\theta_{131-1\bar{3}1}$ at approximately 1.0 wt. % bulk Li_2O content in the 700° C runs and a slightly higher bulk Li_2O content in the runs at higher

¹ The term β -spodumene is not strictly correct as this compound does not have a pyroxene structure. The term is retained here to comply with the usage of other authors (e.g. Skinner and Evans, 1960).

temperature. The lower values for runs of 800 hr at 700°C in comparison to those of 160 hr at the same temperature suggest that equilibrium has not been established in the shorter runs. At this temperature MacKenzie (1957) found that supposed equilibrium values for pure albite

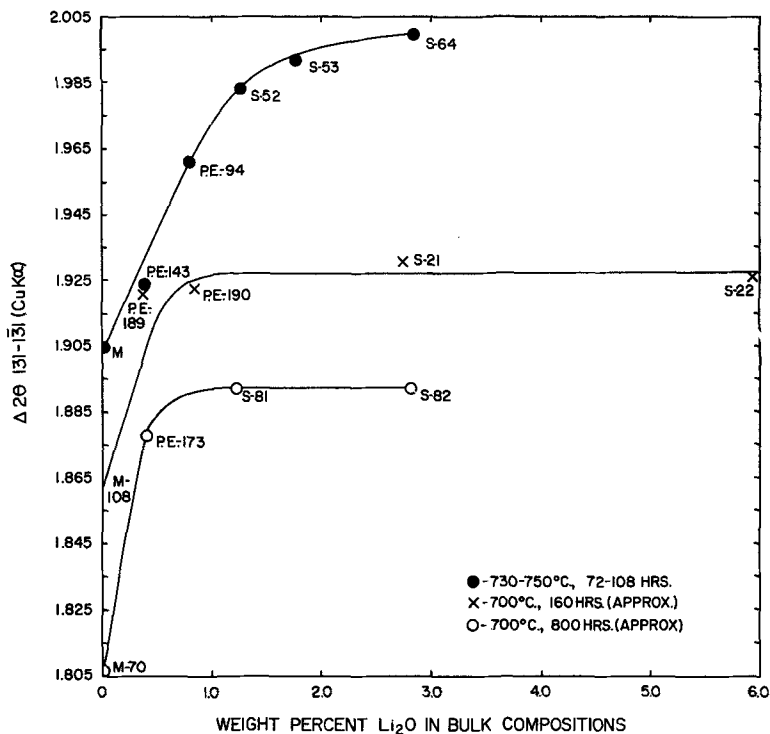


FIG. 1. $\Delta\theta_{131-131}$ plotted against weight % Li_2O in bulk compositions. Data labelled: M from MacKenzie (1957); S from Stewart (1960); P.E. from present study

were not attained in experiments of 1200 hr. Lack of certainty of equilibrium values for pure albite do not permit us to compare data for albites crystallized in the presence of lithium with those of pure albites and thus ascertain that equilibrium in the ordering of albites has been achieved in our experiments.

In his study of pure albites, MacKenzie (1957) concluded that temperature, pressure, time of crystallization, and grain size of the starting material affects the $\Delta\theta_{131-131}$; and that there were an infinite number of intermediate presumed stable forms of albite between the high- and

low-temperature forms. MacKenzie attributed these variations principally to differences in the degree of ordering of silicon and aluminium atoms in the structure. The present study and that of Stewart (1960) show that the addition of lithium raises the value of $\Delta 2\theta_{131-1\bar{3}1}$. Smith and Yoder (1956) have shown that the addition of calcium (as the anorthite molecule) to high-temperature albite does not appreciably affect the $\Delta 2\theta_{131-1\bar{3}1}$. MacKenzie (1957, p. 502) states that the addition of potassium lowers the $\Delta 2\theta_{131-1\bar{3}1}$ value of pure albite.

Increase in the $\Delta 2\theta_{131-1\bar{3}1}$ of albites crystallized in the presence of lithium may be caused either by the effectiveness of lithium in reducing the silicon-aluminium ordering process or by a substitution involving $\text{Li}^+ + \text{Al}^{3+} \rightleftharpoons \text{Si}^{4+}$ or $\text{Li}^+ \rightleftharpoons \text{Na}^+$. Possibly both mechanisms are operative, although neither of these explanations is very satisfactory. The larger separations do not necessarily reflect a difference in the structural states of albite since the addition of potassium has an opposite effect to that of lithium, although the feldspars may have similar structural states to that of pure albite. The substitution mechanisms are also unlikely since a significant volume increase would be involved for the first and a volume decrease for the second.

The change in slope of the curves in fig. 1 may indicate the limit of solid solution of lithium in the feldspar structure. Although 1.0 wt. % Li_2O in the bulk composition is approximately equal to 12.5 wt. % of the spodumene component in the $\text{NaAlSi}_3\text{O}_8$ - β - $\text{LiAlSi}_2\text{O}_6$ system, the amount of lithium in the albite is undoubtedly much lower than this since the coexisting β -spodumene and gas phases are non-stoichiometric with respect to SiO_2 , and possibly with respect to Na_2O and Al_2O_3 (Stewart, 1963, 1964). Optically, β -spodumene crystals were found in the $\text{NaAlSi}_3\text{O}_8$ - β - $\text{LiAlSi}_2\text{O}_6$ - H_2O system at bulk compositions containing as little as 2.5 wt. % of the β -spodumene molecule.

In an attempt to compare the $\Delta 2\theta_{131-1\bar{3}1}$ of the synthetic albites to those of natural albite from lithium-bearing pegmatites, this parameter was kindly determined by Mr. C. W. Armstrong for three samples of albite from a lithium pegmatite from Figuery Township, Quebec. For these samples the values of $\Delta 2\theta_{131-1\bar{3}1}$ ranged from 1.076° to 1.098° . These values are comparable to those of synthetic low albite (MacKenzie, 1957) and to a very pure albite from Tiburon, California, also from a low temperature environment. These results are in accord with the data reported by Boudette (1959) (quoted in Stewart, 1960) for plagioclases from the lithium-bearing Hugo Pegmatite, South Dakota.

Differences in the $\Delta 2\theta_{131-1\bar{3}1}$ separations of synthetic albites crystallized in the presence of lithium and those from natural lithium-rich environments may be explained by the very different structures of the coexisting lithium minerals. In the synthetic systems of the present study, and in Stewart's (1960) investigation, the coexisting minerals are β -spodumene and α -eucryptite respectively, whereas in pegmatites the coexisting lithium mineral is α -spodumene. Skinner and Evans (1960) have shown that the structures of these two modifications of spodumene are radically different. β -spodumene has channels in its structure through which lithium can be readily leached. In contrast α -spodumene has a much tighter pyroxene-type structure in which the cations are strongly bonded. Thus in the synthetic systems lithium ions may enter the albite structure more readily by being leached from the β -spodumene by the aqueous phase. A similar hypothesis may also apply to eucryptite in the synthetic systems where lithium could also be easily leached from this framework-type structure (Winkler, 1948). Available analyses of albites from lithium pegmatites show very low lithium contents (generally less than 0.050 wt. % Li_2O). However, all of these analyses are from samples in which the coexisting lithium mineral is α -spodumene. The presence of a lithium-rich albite from pegmatites containing α -eucryptite as the coexisting lithium mineral would add support to the hypothesis of lithium leaching by the aqueous phase.

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