Stability of K- and Na-Dawsonite

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Introduction

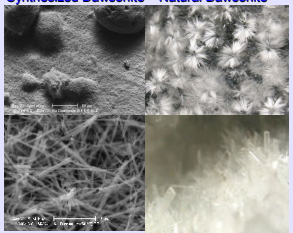
Dawsonite [$Na/KAlCO_3(OH)_2$] is predicted to play an important role in the permanent storage of CO_2. In order to better understand the role of dawsonite in CO_2 mineralization, we are investigating the stability of Na- and K-dawsonite.

Experiments

Synthesis and precipitation studies were made in unstirred, closed Parr™ reaction vessels, saturated in solid bicarbonate and conducted between 50 to 200°C from 1 day to several months. These experiments were supplemented with high-pressure stirred autoclave studies at 75 to 150 °C and 14 MPa for 1 to 14 days. Dissolution studies were conducted in DI water, bicarbonate, NaCl, or HCl solutions at room temperature in stirred vessels for several weeks.

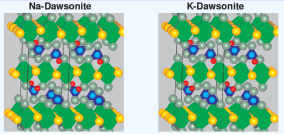
Results and Discussion

Synthesized Dawsonite Natural Dawsonite



Crystal Structure of Dawsonite

Na-Dawsonite K-Dawsonite



	Space Group	Cell Parameter (A) a	b	c	Density (g/cm³)	Volume of Cell (A³)
K-	Cmcm	6.2842	11.9371	5.6287	2.488	422.24
Na-	Imma	6.7708	5.5901	10.4415	2.421	395.21

▲ The K-Dawsonite structure was unknown at the time of this work but was recently published by Fernandez-Carrasco (2005).

Precipitation of Dawsonite from Al-minerals in $NaHCO_3$ Solutions (Na/Al=8)

Reactant	50°C	75°C	94°C	120°C	150°C	200°C
Gibbsite	No Reaction (1day 5.33M)	No Reaction (1day 5.33M) 21%Dawsonite (41days 5.33M)	1% Dawsonite (1day 5.33M)	41% Dawsonite (1day 5.33M)	No Reaction (1day 0.5M) Minor Dawsonite (3days 5.0M) Significant Bohmite (14days 0.5M) Significant Dawsonite (3days 1M) Dawsonite (3days 2M) Significant Dawsonite (1day 5.33M)	Significant Dawsonite (3days 5.33M)
Gibbsite + Quartz	/	No Reaction (7days)	/	/	+ Trace Cancrinilite (7days) Dawsonite + Analcime (20days) Analcime (30days)	Analcime (7days)
Gibbsite + Opal-CT	/	No Reaction (7days)	/	/	Dawsonite + Bohmite (7days) Dawsonite + Bohmite (20days) Analcime + Mordenite (72days)	Analcime + Mordenite + Dawsonite (7days)
Kaolinite	/	Dawsonite + Halloysite (40days)	/	/	Dawsonite + Analcime (60days)	Dawsonite + Albite + Cancrinilite (66days)
Albite	/	No Reaction (40days)	/	/	Minor Analcime (60days)	Significant Analcime (66days)
K-Feldspar	/	/	/	/	Analcime (60days)	/
Analcime	/	/	/	/	No reaction (20days)	/
Pyrophyllite	/	/	/	/	Analcime (20days)	/
Montmorillonite	/	/	/	/	/	Analcime + Albite (66days)
Clinoptilolite	/	/	/	/	/	Analcime + Cancrinilite (66days)

▲ Albite, K-feldspar, pyrophyllite, montmorillonite, and clinoptilolite do not produce dawsonite but react to form analcime. Analcime appears stable in $NaHCO_3$ solution.

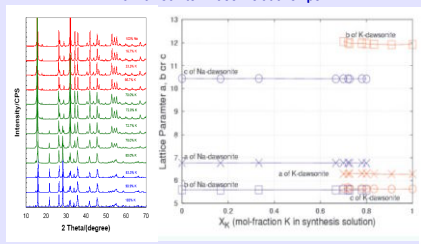
▲ Kaolinite reacts to dawsonite at temperature as low as 75°C.

▲ Gibbsite reacts readily to form dawsonite but is sensitive to presence of silica.

Synthesis of Dawsonite in the High-Pressure Stirred Autoclave

Reactants	50°C	150°C
$NaHCO_3$<1M		No Reaction 2.7 days
$NaHCO_3$>1M		Dawsonite, 2.7 days
0.5M $NaHCO_3$+0.5M NaCl		Dawsonite, 2.9 days
NaCl>1M		No Reaction, 2.7 days
1M NaCl+Calcite		No Reaction, 2 days
1M NaCl+Calcite	No Reaction 14 days	

K/Na-Dawsonite Phase Relationships



▲ Only essentially pure K/Na-dawsonite forms in this system.

▲ In the region between 70 and 80% $KHCO_3$, K- and Na-dawsonite co-exist.

▲ The x-ray diffraction data are supported by bulk chemical analysis of synthesized products (e.g. at X_K=33% or 91%) that show there is essentially no solid solution between K- and Na-dawsonite.

References

Fernandez-Carrasco, L., Puertas, F., Blanco-Varela, M. T., Vazquez, T. and Rius J. (2005) Synthesis and crystal structure solution of potassium dawsonite: An intermediate compound in the alkaline hydrolysis of calcium aluminate cements. Cement and Concrete Research, 35, 641-646.

Acknowledgements

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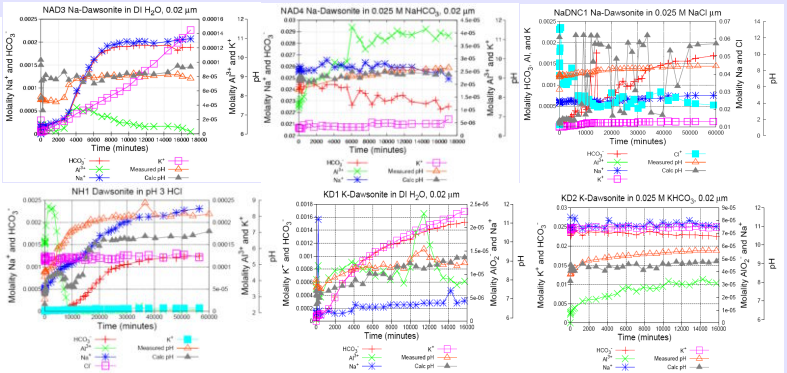
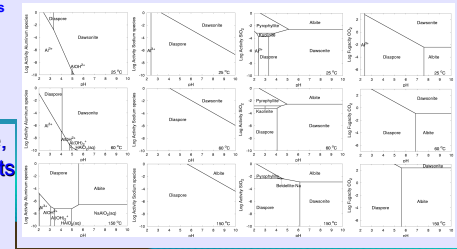
Dissolution of K/Na-Dawsonite in DI water, bicarbonate, NaCl, or HCl solutions



▸ Geochemical Modeling of Dawsonite Stability (Geochemist's Workbench™)

Geochemical modeling of dawsonite shows that it has a wide stability in $NaHCO_3$ solutions at intermediate pH (4-11). Its stability field decreases with temperature and, interestingly, with increased silica activity. In the calculated diagrams, activities for species held constant were Al^{3+} = albite, Na^+ = 1, SiO_2 = quartz, and CO_2 = 75 bars.



Conclusions

Na- and K-dawsonite were readily synthesized from $(Na,K)HCO_3$ and gibbsite ($Al(OH)_3$) at 150°C. Other Al-bearing minerals including albite, K-feldspar, and montmorillonite showed no evidence of dawsonite. Synthesis with gibbsite at a P_{CO_2} of 14 MPa also produced dawsonite. Synthesis experiments with gibbsite-silica were significantly different from gibbsite alone. There was no solid solution between the Na- and K-endmembers of dawsonite, which co-precipitated at $0.68 \le X_{KHCO_3} \le 0.80$. The apparent solubility of dawsonite was greater in bicarbonate solution compared to DI, NaCl, and HCl solutions.