ROEDDER, E. (1951) The system K_2O-MgO-SiO_2. *Amer. J. Sci.* **249,** 224.

SCHREYER, W., AND J. SCHAIRER (1962) Metastable osumilite- and petalite-type phases in the system MgO-Al_2O_3-SiO_2. *Amer. Mineral.* **47,** 90.

SMITH, J. (1965) X-ray emission microanalysis of rock-forming minerals I. Experimental techniques. *J. Geol.* **73,** 830.

——— (1966) X-ray emission microanalysis of rock-forming minerals VI. Clinopyroxenes near the diopside-hedenbergite join. *J. Geol.* **74,** 463.

———, and P. RIBBE (1966) X-ray emission microanalysis of rock-forming minerals III. Alkali feldspars. *J. Geol.* **74,** 197.

TANEDA, S. (1950) Cordierite-bearing "ash stone" around the Bay of Kagoshima. *Stud. Fac. Sci. Kyushu Univ., Sec. Geol.* **2,** 47.

THE AMERICAN MINERALOGIST, VOL. 52, SEPTEMBER-OCTOBER, 1967

SYNTHESIS OF CALCIOGADOLINITE

JUN ITO, *Department of Geological Sciences, Harvard University, Cambridge, Massachusetts.*[1]

Previous studies of synthetic gadolinite, $Fe^{+2}Y_2Be_2Si_2O_{10}$, by the writer (1965, 1966) have demonstrated that this mineral can form numerous solid solution series involving the replacement of Fe^{2+} and Y^{3+} by other divalent and trivalent metals respectively. The crystallographic properties and chemical stabilities of the resulting synthetic phases were also shown to vary systematically with the ionic radii of the elements involved in these substitutions. These investigations have now been extended to include the calciogadolinites.

Calciogadolinite, containing 11.9 weight percent CaO, was first described by T. Nakai (1938) from the pegmatite of Tadachi, Nagano, Japan. Nearly all other chemical analyses of natural gadolinite similarly report CaO in amounts that commonly range up to 3 weight percent (Dana, 1892), (Nagashima, 1960). The role of this calcium remained uncertain because of the possibility of admixed impurities in the samples analyzed and the unknown extent to which calcium could be incorporated into the gadolinite structure. The fact that the calcium reported in these analyses is frequently accompanied by ferric iron in an approximately 1:1 mole ratio, however, does suggest the presence of a solid solution series involving the partial replacement of Y^{3+} by Ca^{2+} with valence compensation being achieved by the concomitant substitution of Fe^{3+} for Fe^{2+} according to the general formula $(Fe_{1-X}^{2+}Fe_X^{3+})(Y_{2-X}Ca_X)Be_2Si_2O_{10}$. The calcium-rich end member of this series should contain a maximum of 13.38 weight percent CaO. Such calciogadolinite and several of its

---

Mineralogical Contribution No. 529.

[1] Present address: National Bureau of Standards, Washington, D. C. 20234.

analogues have been synthesized and characterized in the present work.

The synthesis of iron calciogadolinites having the formulas $Fe^{3+}CaYBe_2Si_2O_{10}$ and $Fe^{3+}CaLaBe_2Si_2O_{10}$ was achieved by using slight modifications of the method previously described by the writer (1965). In addition, an iron free, gallium calciogadolinite having the formula $GaCaYBe_2Si_2O_{10}$ was similarly obtained but attempts to replace the iron in calciogadolinite by Cr^{+3}, Al^{3+} and Sc^{3+} failed. Attempts to replace yttrium in ferrous gadolinite by scandium also proved unsuccessful.

The synthesis of the calciogadolinites consisted of heating silicate gels containing the necessary elements in their stoichiometric proportions at a temperature of 1150°C for a period of 20 hours in air. Unlike acid insoluble silica gels that have conventionally been used as starting materials, the starting material used in the present study consisted of the far more reactive and homogeneous acid soluble *silicate* gels. These gels were prepared by adding NH_4OH to slightly acidic, 150 ml solutions containing 1.0 millimole of ferric nitrate (or gallium chloride) and yttrium chloride (or lanthanum chloride) plus 2.0 millimole of beryllium nitrate, sodium silicate and calcium nitrate. The pH of the solution was adjusted to a value of 10.0 by adding excess NH_4OH. The resulting gelatinous precipitate was centrifuged, washed with distilled water, oven dried at 110°C and then pulverized into a fine powder. The one millimole excess calcium used in this procedure was added to compensate for its incomplete precipitation by NH_4OH. Partial chemical analysis of the gels produced showed that they contained the desired elements in their stoichiometric proportions.

The identification and characterization of the synthetic calciogadolinite were accomplished by X-ray diffraction and optical techniques and by partial chemical analysis. Optically, the successfully synthesized phase was seen to approximate 90 percent of the total reaction product. The ferric calciogadolinite occurred as aggregates of light brown, transparent crystals. The gallium calciogadolinite also occurred as small, transparent but colorless crystals.

Precise determinations of the refractive indices of these phases could not be made because of their small particle size. Their mean indices of refraction, however, all occurred in the range 1.75–1.80. X-ray diffraction patterns of the synthetic calciogadolinites were obtained with a diffractometer using Cu radiation and a nickel filter. These patterns all closely corresponded to those of natural gadolinite although they did contain several extraneous peaks due to the minor impurities present such as lessingite and abukumalite. Table 1 lists the indexed d values, unit cell constants and β angles calculated on the basis of the crystal lattice by Ito and Mori (1952).

TABLE 1. X-RAY AND EXPERIMENTAL DATA FOR CALCIOGADOLINITE

Formula	$Fe^{+3}CaLaBe_2SiO_{10}$		$Fe^{+3}CaYBe_2Si_2O_{10}$		$Ga^{+3}CaYBe_2Si_2O_{10}$	
CaO	n.d.		14.1%		n.d.	
Unit cell constants	(Å)		(Å)		(Å)	
a	4.76		4.69		4.67	
b	7.75		7.56		7.57	
c	10.15		9.97		9.99	
β	90.5°		90.0°		90.0°	
hkl	*d*	*I*	*d*	*I*	*d*	*I*
100	4.76	80	4.69	40	4.67	50
012	4.26	10	4.10	5	4.11	10
$11\bar{1}$	3.88	3			3.79	5
021	3.619	30	3.531	10	3.545	10
102	3.448	5	3.424	8	3.406	10
$11\bar{2}$	3.182	50	3.118	100	3.108	90
112	3.155	60				
013	3.101	50	3.046	30	3.052	40
120	3.005	60	2.945	60	2.943	80
121	2.880	100	2.825	70	2.825	100
$11\bar{3}$	2.608	30	2.559	80	2.553	100
113	2.587	60				
014	2.414	10	2.372	5	2.373	10
200	2.378	10	2.345	10	2.335	15
210	2.301	20	2.252	10	2.256	10
211	2.215	5	2.169	8	2.203	10
024	2.074	5	2.030	5	2.029	10
221	1.988	20	1.955	10	1.947	10
$22\bar{2}$	1.894	20	1.857	40	1.857	20
222	1.879	10				

All at 1150°C, 1 atm., 20 hrs.

The results of the present work have been combined with those obtained from the writer's previous study of synthetic gadolinite (1965) and are summarized in Figure 1. This figure illustrates the great variety of elements that can isomorphously replace Fe^{2+} and Y^{3+} in the gadolinite structure. Natural gadolinite has long been recognized as a non-selective rare earth mineral due to the ability of its Y^{3+} sites to accommodate all 15 trivalent lanthanide elements in their natural proportions (Goldschmidt and Thomassen, 1924). In addition to confirming the flexibility of the Y^{3+} site, these investigations of synthetic gadolinite have shown that the Fe^{2+} position in this mineral is also extremely flexible. As shown in Figure 1, ferrous iron can be completely replaced by divalent Cd, Mn, Cu, Zn, Co, Ni, Mg and by trivalent Fe and Ga. Also, the successful

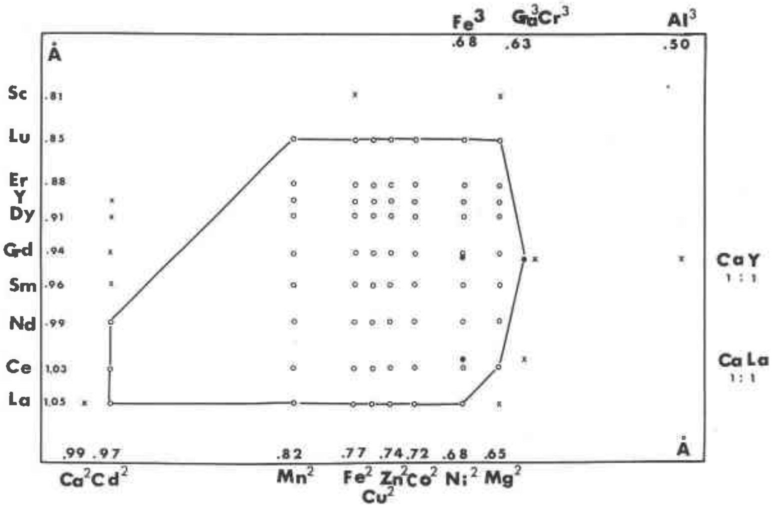

FIG. 1. Region of chemical stability of gadolinite in terms of the ionic radii of the divalent cations and rare earths occupying sites in the gadolinite structure. Rare earth radii from Templeton (1954), other radii from Wells (1962). Open circles = gadolinite; black circles = calciogadolinite; crosses = other phases.

synthesis of calciogadolinite has demonstrated that Ca can occupy up to one half the Y^{3+} sites in the gadolinite structure. This result supports the conclusion that the calcium reported in natural gadolinite samples, when accompanied by appropriate amounts of ferric iron or other valence compensating elements, is incorporated within the crystal structure of this mineral and is not necessarily due to the presence of admixed impurities in the samples analyzed.

The writer is indebted to his colleague, William Sabine, for his help in revising the original manuscript of this note, and to Professor C. Frondel of Harvard University and Dr. F. E. Wickman for critical reading of the manuscript.

REFERENCES

DANA, E. S. (1892) System of Mineralogy, 6th Edition, Wiley, New York, p. 507.

GOLDSCHMIDT, V. M. AND I. THOMASSEN (1924) Geochemische Verteilungsgesetze der Elemente. III, Roentgenspektrographische Untersuchungen über die Verteilung der seltenen Erdmetalle in Mineralien. *Videnskapsselsk. Skr. I. Mat.-Naturviss. Klasse*, no. 5.

ITO, JUN (1965) The synthesis of gadolinite. *Proc. Jap. Acad.*, **41**, 404–407.

——— (1966) A note on the gadolinite synthesis. *Proc. Jap. Acad.*, **42**, 634–635.

ITO, TEIICHI AND H. MORI (1963) The crystal structure of datolite. *Acta Crystallogr.* **6**, 24–32.

NAGASHIMA, OTOKICHI AND K. NAGASHIMA (1960) *Rare elements minerals from Japan.* Japan Mineral Club Press, Kyoto, Japan, p. 184–189.
NAKAI, TOSHIO (1938) On calciogadolinite, a new variety of gadolinite found in Tadachi, Nagano, Japan. *Bull. Chem. Soc. Jap.*, **13,** 591–594 [Mineral. Abstr. **7,** 264 (1939)].
TEMPLETON, D. H. AND D. H. DAUBEN (1954) Lattice parameter of some rare earth compounds and a set of crystal radii. *J. Chem. Soc.* **76,** 5237.
WELLS, A. F. (1962) *Structural Inorganic Chemistry.* 3rd ed., Oxford Press, Oxford, p. 483.

THE AMERICAN MINERALOGIST, VOL. 52, SEPTEMBER-OCTOBER, 1967

BIAXIAL CALCITE INVERTED FROM ARAGONITE

A. L. BOETTCHER AND P. J. WYLLIE, *Department of the Geophysical Sciences, The University of Chicago.*

INTRODUCTION

We have recently extended the phase relationships involving a liquid phase in the system CaO-CO_2-H_2O from 4 kilobars pressure (Wyllie and Tuttle, 1960; Wyllie and Raynor, 1965) to 40 kilobars pressure (to be published). Under appropriate conditions the phase assemblage calcite +liquid+vapor undergoes a transition to aragonite+liquid+vapor. Published data indicate that the calcite-aragonite transition curve should intersect the ternary univariant solidus curve at about 580°C at a pressure between 11.5 and 13 kilobars. At temperatures above 600°C, Bell and England (1964) concluded that the aragonite which formed stably within a wide pressure interval inverted to calcite during the quench. Thus, quenching problems have apparently contributed to the conflicting reports for the position of the calcite-aragonite phase transition. Examination of the morphology of the carbonate in the quenched assemblage $CaCO_3$+liquid+vapor suggested a method for locating the calcite-aragonite transition boundary regardless of the polymorphic changes that may occur during the quench.

THE CALCITE-ARAGONITE PHASE TRANSITION

The liquid in the ternary system CaO-CO_2-H_2O is a very reactive medium, and during the investigation of this system and of a variety of related systems no problems have been encountered in reaching equilibrium (Wyllie, 1966).

In runs completed at pressures well above and below the aragonite-calcite transition boundary, aragonite and calcite crystals in the assemblage $CaCO_3$+liquid+vapor were positively identified by X ray and optical properties. The morphology of the aragonite crystals in equi-