THE AMERICAN MINERALOGIST, VOL. 53, SEPTEMBER-OCTOBER, 1968

SYNTHETIC INDIUM SILICATE AND INDIUM HYDROGARNET

JUN ITO, *National Bureau of Standards, Washington, D. C. 20234.*

ABSTRACT

The following indium silicates were synthesized hydrothermally and in air: indium grossular, $Ca_3In_2Si_3O_{12}$; indium aegirine, $NaInSi_2O_6$; indium beryl, $Be_3In_2Si_6O_{18}$; indium thortveitite, $In_2Si_2O_7$; indium melanotekite, $Pb_2In_2Si_2O_9$; and strontium indium hydrogarnet, $Sr_3In_2(OH)_{12}$.

Complete solid solubility was found between ferric iron and indium silicates and hydrogarnet end members. Single crystals of indium aegirine up to 2 cm in length were grown in a Na_2WO_4 flux by slow cooling.

The crystal chemical and geochemical behavior of trivalent indium is similar to that of scandium. The ionic radius of trivalent indium of 0.81 Å given by Pauling is confirmed.

INTRODUCTION

The oxide systems containing indium oxide have been studied lately (Keith and Roy, 1954; Roth and Schneider, 1960; Shannon, 1967). The systems, however, containing silica and indium oxide have not been systematically studied. Only an indium aegirine as an impurity in the hydrothermal synthesis of indium oxide (Christensen, Brock, and Hazel, 1967) and indium grossular (Mill, 1964) were reported. The average concentration of indium in common silicate rocks was determined as approximately 0.1 ppm (W-1 0.094 ppm and G-1 0.042 ppm, Brooks and Ahrens, 1961). In the earth's crust, indium occurs commonly with sulfides and cassiterite, SnO_2. Three indium minerals, indite ($FeIn_2S_4$, Genkin and Muravéva, 1963), roquesite ($CuInS_2$, Picot and Pierrot, 1963) and sakuraiite, [$(Cu,Fe,Zn,Ag)_3$ (In,Sn) S_4, Kato, 1965] are all sulfides. The only other indium mineral is the hydroxide dzhalindite, In $(OH)_3$, an alteration product of indite (Genkin and Muravéva, 1963). No indium silicate has been reported in nature.

Frondel and I reported work on the synthesis of scandium silicates, such as Sc-garnet, Sc-hydrogarnet, Sc-beryl, Sc-aegirine, and Sc-melanotekite (Frondel and Ito, 1968; Ito and Frondel, 1968). We established the presence of complete solid-solution series between Sc-silicates and hydrogarnet, and ferric iron silicates and ferric hydrogarnet. I have subsequently used the same approach for the syntheses of indium analogues, because the trivalent ionic radii of indium and scandium are similar. All the indium analogues, including In-beryl and In-thortveitite, are obtained under nearly the same conditions as the corresponding scandium compounds.

The systems In-aegirine$\rightleftarrows$aegirine, In-grossular$\rightleftarrows$andradite, In-melanotekite$\rightleftarrows$melanotekite and In,Sr-hydrogarnet$\rightleftarrows$Fe,Sr-hydrogarnet were introduced. The results, the method of the syntheses and the unit-cell dimensions for the new compounds are given.

METHOD OF PREPARATION AND EXPERIMENTAL RESULTS

Gel preparation. The following CP-grade reagents were used for the syntheses: sodium silicate, strontium-, calcium-, lead-, chromium- and aluminum nitrates, manganese chloride, ammonium vanadate, gallium-, scandium- and indium oxides, ammonium carbonate, ammonium and sodium hydroxides, ascorbic and hydrochloric acids.

The starting gel for indium aegirine was prepared by mixing hydrated indium silicate and sodium silicate solution ($Na_2SiO_3+In_2Si_3O_9\cdot nH_2O=2\ NaInSi_2O_6+nH_2O$). The smooth gelatinous mixture was dried slowly at 105°C in a porcelain evaporating dish.

The gel for indium calcium garnet was prepared at pH 9 by adding ammonia and ammonium carbonate to a solution containing stoichiometric amounts of calcium nitrate, indium chloride and sodium silicate.

The co-precipitated mixture was washed, centrifuged and air dried. The dried gel was pulverized and mixed well in order to avoid segregation of crystalline carbonate.

The gels for indium-melanotekite, thortveitite, and beryl were prepared by precipitation from stoichiometric solution with ammonia at the boiling point (pH 9). The sodium absorption in the gels was minimized easily by repeated precipitation under the same conditions. Unlike other silica gels used conventionally, the precipitates are acid soluble and the components of these compounds are precipitated quantitatively by ammonia.

Compound synthesis and examination. Hydrothermal syntheses of the compounds were carried out in the 25 ml cold seal steel bombs at temperatures from 450 to 720°C and under 1.5 to 2 kbars pressure. Calculated amounts of water were added to produce the desired water pressure. Silver liners 2.5 cm long and 3 mm OD made of 0.03 mm silver foil, were used as specimen containers. Heating was usually limited to 48 hours. In other instances, gels were heated in air up to 1,200°C, in a platinum foil and air quenched.

All the synthetic products were examined by the X-ray powder diffraction method with Cu K radiation and Ni filter and petrographic microscopic technique. Unit-cell dimensions were calculated according to the known space groups, and are given in Table 1 with the experimental conditions.[1]

Indium silicates. Calcium indium garnet is colorless and under the microscope gives small round isolated crystals up to 5μm in size. They decompose to In_2O_3 and an unidentified calcium silicate at 1080°C. The refractive index is 1.760.

Indium melanotekite appears as a fine powder but not as the euhedral crystals obtained with melanotekite (Ito and Frondel, 1966) by hydrothermal crystallization. This synthesis is also achieved by heating in air at 950°C. The compound decomposes to an unidentified phase before melting occurs incongruently at 1090°C.

Beryl, $Be_3In_2Si_6O_{18}$, is obtained hydrothermally at temperatures from 420–600°C under 2–3 kbar pressure. A pure single-phase sample has not been obtained. It is always accompanied by small amounts of an un-

---

[1] X-ray powder diffraction data have been submitted to the ASTM Powder Diffraction File.

TABLE 1. UNIT-CELL DIMENSIONS AND EXPERIMENTAL CONDITIONS FOR THE SYNTHETIC INDIUM SILICATES AND HYDROGARNETS

	Formulas	T(°C)	p(kbar)	a	b	c	β
In aegirine monoclinic $C2/c$	$NaInSi_2O_6$	720 1200–750	2 in air using flux	9.88	9.13	5.38	107.3
	$Na(Fe_{.25}In_{.75})Si_2O_6$	720	2	9.85	9.05	5.36	107.5
	$Na(Fe_{.50}In_{.50})Si_2O_6$	720	2	9.78	8.93	5.35	107.5
	$Na(Fe_{.75}In_{.25})Si_2O_6$	700	2	9.73	8.87	5.32	107.5
	$Na(In_{.50}Sc_{.50})Si_2O_6$	720	2	9.85	9.09	5.38	107.3
In melanotekite orthorhombic $C222_1$	$Pb_2In_2Si_2O_9$	900 500	in air 2	7.02	11.39	10.54	—
	$Pb_2(Fe_{.25}In_{.75})_2Si_2O_9$	550	2	7.02	11.31	10.45	—
	$Pb_2(Fe_{.50}In_{.50})_2Si_2O_9$	550	2	6.99	11.23	10.36	—
	$Pb_2(Fe_{.75}In_{.25})_2Si_2O_9$	550	2	6.97	11.13	10.24	—
In garnet isometric, $Ia3d$	$Ca_3In_2Si_3O_{12}$	575	2	12.36	—	—	—
	$Ca_3(Fe_{.25}In_{.75})_2Si_3O_{12}$	620	2	12.28	—	—	—
	$Ca_3(Fe_{.50}In_{.50})_2Si_3O_{12}$	620	2	12.21	—	—	—
	$Ca_3(Fe_{.75}In_{.25})_2Si_3O_{12}$	620	2	12.15	—	—	—
	$Ca_3(In_{.50}Sc_{.50})_2Si_3O_{12}$	620	2	12.30	—	—	—
In beryl hexagonal, $P6/mcc$	$Be_3In_2Si_6O_{18}$	550	2	9.70	—	9.172	—
	$Be_3(In_{.75}Fe_{.25})_2Si_6O_{18}$	550	2	9.52	—	9.13	—
In thortveitite monoclinic, $C2/m$	$In_2Si_2O_7$	680 1150	2 in air	6.63	8.63	4.69	102.8
Sr-In-hydrogarnet isometric, $Ia3d$	$Sr_3In_2(OH)_{12}$	115	in air	13.522	—	—	—
	$Sr_3(Fe_{.25}In_{.75})_2(OH)_{12}$	115	in air	13.44	—	—	—
	$Sr_3(Fe_{.50}In_{.50})_2(OH)_{12}$	115	in air	13.38	—	—	
	$Sr_3(Fe_{.75}In_{.25})_2(OH)_{12}$	115	in air	13.28	—	—	—
	$Sr_3(In_{.50}Sc_{.50})_2(OH)_{12}$	115	in air	13.46	—	—	—

identified crystalline phase. The crystals are submicroscopic. The decomposition temperatures of In-beryls can be raised by the addition of small amounts of ferric iron and sodium. Sodium ions probably stay in the hexagonal channels of beryl; ferric iron may replace both silicon in the rings and indium at the cation sites between the rings. Unit-cell dimensions are slightly larger than those of scandium beryl.

Indium pyrosilicate was obtained by heating in air and also hydrothermally. It is isostructural with thortveitite, and therefore isostructural with β-$Y_2Si_2O_7$ (Ito and Johnson, 1968). Unit-cell dimensions were calculated according to the space group $C\ 2/m$. The crystals were too small for detailed microscopic observation.

Growth of indium aegirine. Indium aegirine crystallized hydrothermally appearing as very fine acicular crystals.

Single crystals of $NaInSi_2O_6$ were grown by slow cooling in a saturated flux of Na_2WO_4 from 1,200 to 800°C. The charge was as follows: In_2O_3 0.50 g; SiO_2 0.72 g and $Na_2WO_4 \cdot 2H_2O$ 50 g. After soaking at 1200°C for 48 hours, the solution was cooled at the rate of 1°C per hour. The crystals obtained are transparent, doubly-terminated and elongated parallel to c up to 2 cm. Faces identified are $\{001\}$ $\{100\}$ $\{110\}$ $\{010\}$ and possibly $\{111\}$. The refractive indices (biaxial) are $\gamma = 1.693$, $\alpha = 1.688$. It melts at approximately 1140°C, probably incongruently.

Hydrogarnet. Strontium indium hydrogarnet was synthesized in fluorocarbon polymer beakers by rapid precipitation from highly alkaline solution (NaOH 1N) containing stoichiometric amounts of indium chloride and strontium nitrate. Fast adjustment of the solution to pH 13.5 is essential to obtain a well stabilized single phase. The solution was kept boiling for 3 hours at 115°C with occasional addition of water, and then aged for 20 hours at 100°C. The final products were centrifuged, washed once with 5 percent ammonia and then with methyl alcohol, and air dried. Glass beakers were not used because Si contamination causes the formation of a second hydrogarnet phase containing Si^{4+} ions, simultaneously with the desired hydrogarnet. Fresh NaOH solution is essential, because the formation of $SrCO_3$ leads to a Sr^{2+} deficient environment, resulting in a very poor yield and even a second phase.

Strontium indium hydrogarnet appears as extremely fine crystals mixed with some unreacted amorphous compound. Measurement of the refractive index was not successful. Once crystallized, it is stable up to 550°C under 2 kbar, and decomposes to unidentified compounds at 650°C under 2 kbar. In air it is stable only up to 150°C.

Solid solubility of indium and ferric iron. Solid solution between Sc^{3+} and In^{3+} compounds has been well known (Schneider, Roth and Waring, 1961). However, only partial solid solubility was reported between In^{3+} and Fe^{3+} end compositions (Ibid. Geller, Williams and Sherwood, 1961) (Maguire and Green, 1967). At high pressure the system Fe_2O_3-In_2O_3 is said to form a complete solid-solution series. This study showed that complete solid solution series exist in the system In-aegirine$\rightleftarrows$aegirine, In-grossular$\rightleftarrows$andradite, In-melanotekite$\rightleftarrows$melanotekite, and In-Sr hydrogarnet$\rightleftarrows$Fe-Sr hydrogarnet. Unit-cell dimensions appear to vary almost linearly as a function of the chemical compositions (Figures 1, 2, 3, and 4). A two-phase region may exist in the garnet series at atomic ratios of Fe to In of about 3:1, although this is not shown in Figure 1. Complete solid solubility may exist in the ternary system In-Sc-Fe for all the above-mentioned compounds.

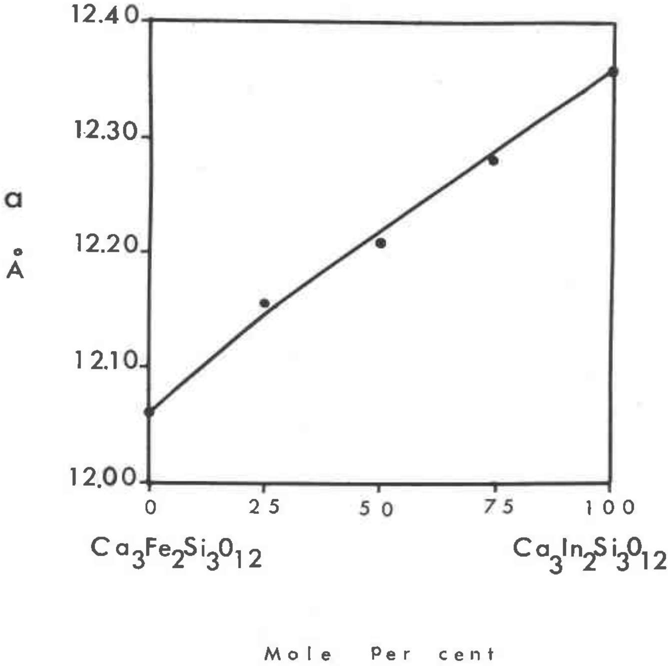

FIG. 1. Unit-cell dimensions for solid-solution series of $Ca_3Fe_2Si_3O_{12}$-$Ca_3In_2Si_3O_{12}$.

DISCUSSION

Ionic radius of indium. The published values for the ionic radius of In^{3+} vary from 0.77 Å (Roth and Schneider, 1960) to 0.92 Å (Goldschmidt, 1937). The unit-cell dimensions or cube roots of unit-cell volumes of all the analogues are plotted against their ionic radii[1] given by Wells (1962) for six-coordinated trivalent ions (Figure 5) with the exception of rare earth radii and the radius for In^{3+}. All the compounds were synthesized in our laboratory, except jadeite, Sr-Al, Sr-Cr, and Sr-Ga hydrogarnet (Schwarz, 1967). Since the next trivalent ion larger than In^{3+} is Lu^{3+}, attempts were made to synthesize small-ion rare earth (Lu, Yb, Tm, and Er) analogues of the above compounds. Only Lu^{3+} and Yb^{3+} analogues of strontium hydrogarnets, and Lu, Yb, Tm, Er, and Ho analogues of thortveitite were obtained. Unit-cell dimensions of the former and cube roots of cell volumes of the latter compounds were also plotted in the same diagram. The value of 0.81 Å given by Wells (1962) for Sc^{3+} had to

---

[1] The following radii values were used throughout this study: Al^{3+} 0.50 Å, Ga^{3+} 0.62 Å, Cr^{3+} 0.64 Å, V^{3+} 0.66 Å and Fe^{3+} 0.68 Å by Wells (1962); In^{3+} 0.81 Å by Pauling (1960); Sc^{3+} 0.76 Å by Frondel and Ito (1967); Lu^{3+} 0.848 Å, Yb^{3+} 0.858 Å, Tm^{3+} 0.869 Å, Er^{3+} 0.881 Å, and Ho^{3+} 0.894 Å by Templeton and Dauben (1954).

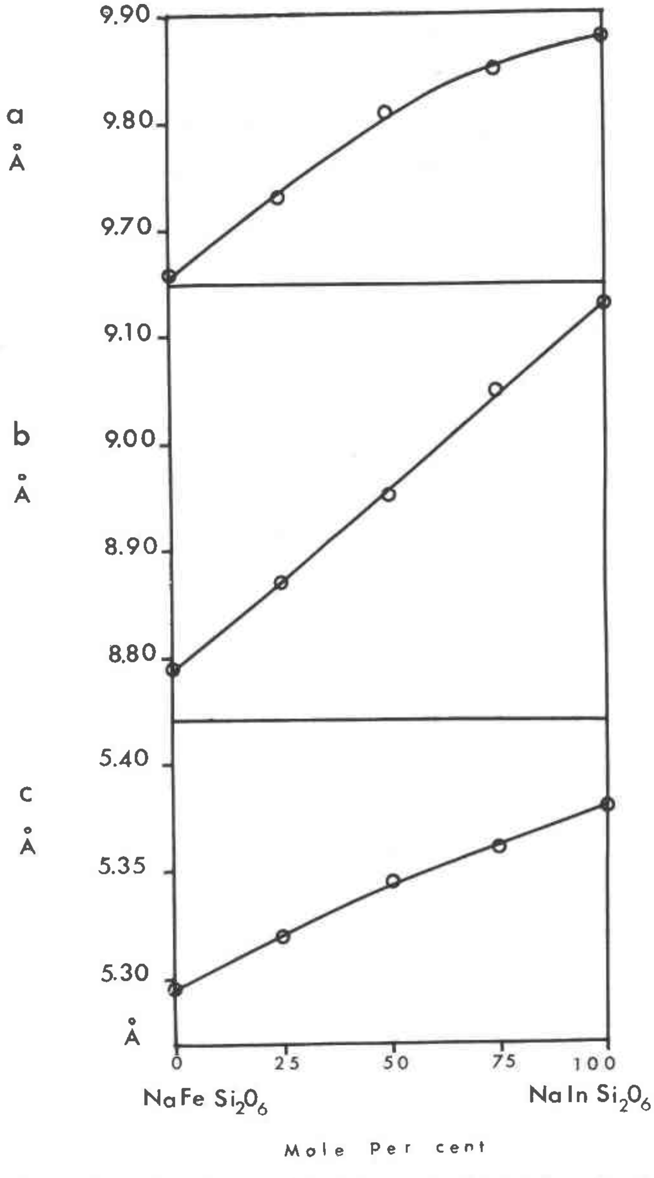

FIG. 2. Unit-cell dimensions for solid-solution series of $NaFeSi_2O_6$-$NaInSi_2O_6$.

be replaced by the revised value of 0.76 Å (Frondel and Ito, 1967) to account for the differences in unit-cell dimensions plotted in this diagram (Figure 5). The ionic radius for In^{3+} based on the data presented here is close to 0.81 Å previously given by Pauling (1960).

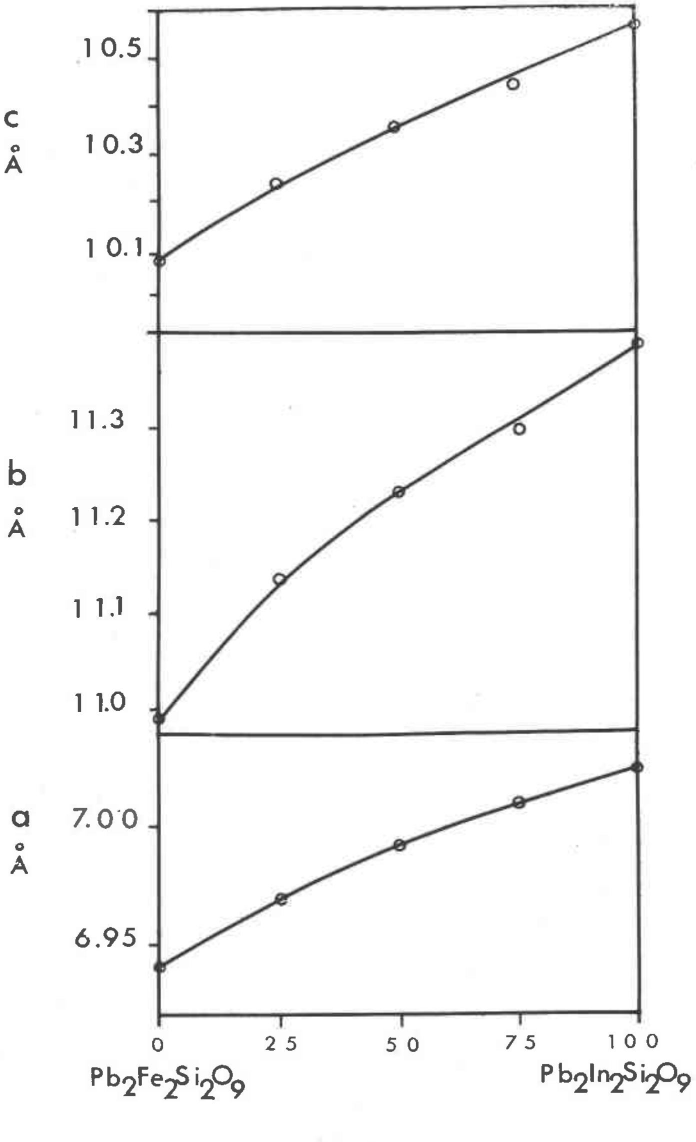

FIG. 3. Unit-cell dimensions for solid-solution series of $Pb_2Fe_2Si_2O_9$-$Pb_2In_2Si_2O_9$.

Some examples of Indium substitution in nature. Indium often occurs in nature in appreciable concentration in sulfides or tin oxide. Spectrographic analysis has shown (Shaw, 1952) that indium also occurs in

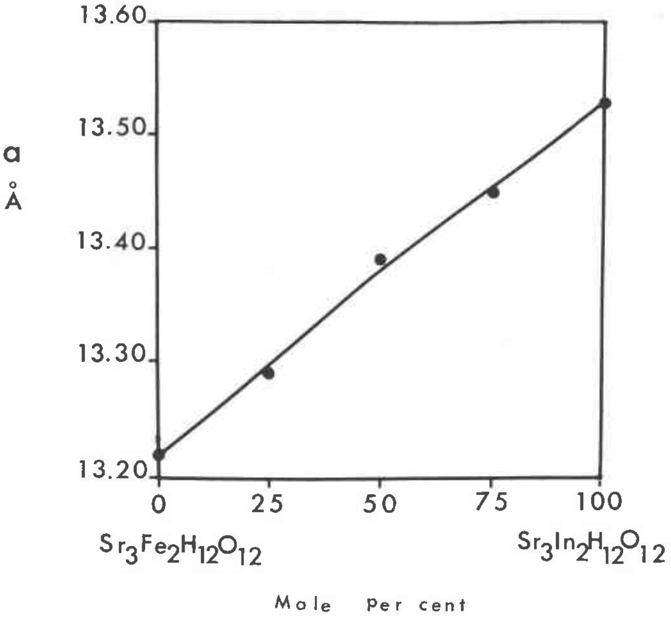

FIG. 4. Unit-cell dimensions for solid solution series of $Sr_3Fe_2(OH)_{12}$-$Sr_3In_2(OH)_{12}$.

small amounts in other minerals, notably in igneous iron, manganese, and aluminum minerals and in sedimentary iron ores.

In fact, indium is a widely distributed element in the earth's crust (Goldschmidt, 1937; Rankama and Sahama, 1950, Erämaetsä, 1938; Ivanov, 1963). There has been disagreement as to whether indium ions are present in solid solution in the principal minerals, or contained as inclusions in sulfides and metallic elements. Goldschmidt (1937) interpreted trace concentration of indium in basic silicate rocks and in zinc sulfides as replacement by In^{3+} ions of lower valency ions such as Fe^{2+}, Mn^{2+}, Zn^{2+}, and Mg^{2+} having the similar ionic radii. Most of the later literature on indium geochemistry followed this interpretation.

Shaw (1952) indicated that indium occurs in most Mg and Fe silicates in low concentration. He stated that his results do not entirely conflict with Goldschmidt's concept. However, I believe some of his results are inconsistent with Goldschmidt's interpretation. He found a noticeable concentration of indium in minerals containing Fe^{3+} and Al^{3+}; hornblende, 5.8 ppm; epidote, 0.59 ppm; muscovite, 4.5 ppm; garnet gneiss, 1.8 ppm and garnetiferous schist, 0.46 ppm. These amounts are significantly higher than the average concentration in common silicate rocks (0.1 ppm).

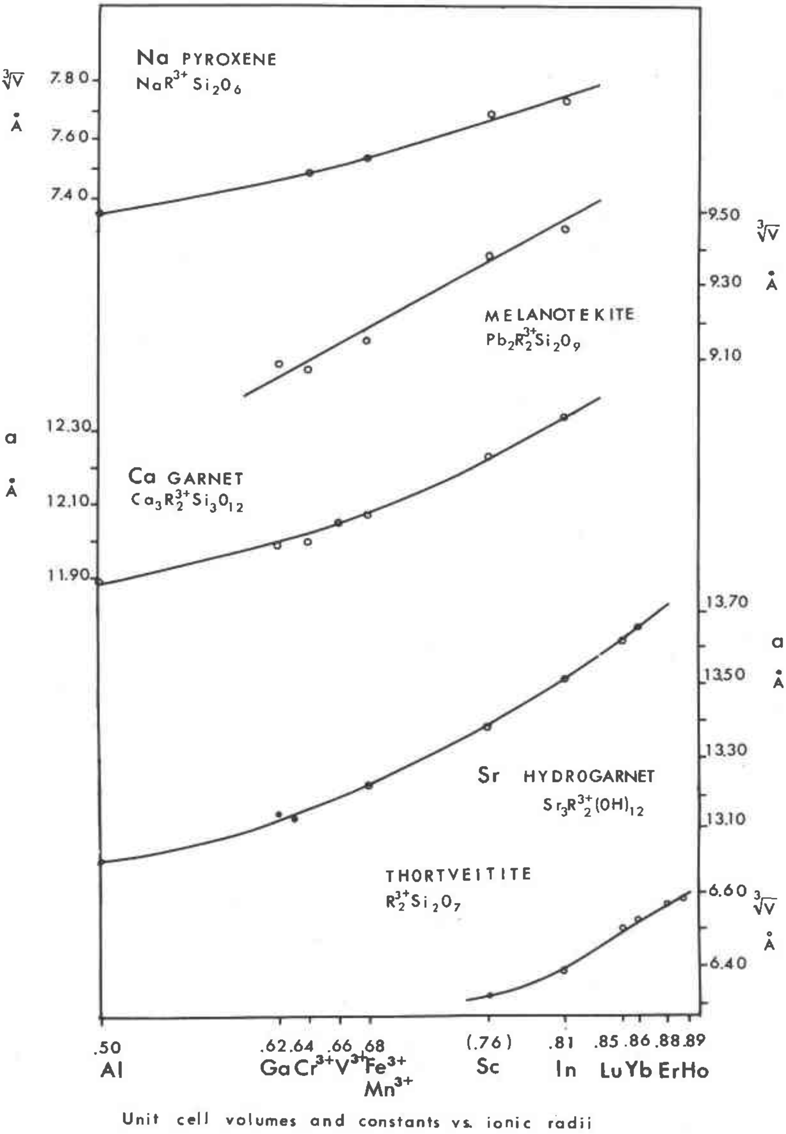

FIG. 5. Unit-cell dimensions of all analogues of the indium compounds versus trivalent ionic radii.

V = The unit cell volume for nonisometric crystals.
a = The unit cell dimensions for isometric crystals.

The theory of isomorphous substitution of In^{3+} (6 coordinated) in octahedral sites of the common trivalent Fe^{3+} or Al silicates should be reconsidered. Substitution of In_2O_3 in Fe_2O_3 is well known (Schneider, Roth and Waring, 1961). The results of this investigation suggest the wide applicability of $In^{3+} \rightleftarrows Fe^{3+}$ substitution for the geochemical interpretation of In concentrations in certain silicates. The majority of indium concentrations previously found in igneous iron silicates, such as in the garnets, epidotes, vesuvianites, beryls, biotites and cordierite, and also in sedimentary limonites and hematites could then be interpreted as a substitution of In^{3+} in trivalent octahedral Fe^{3+} sites. Goldschmidt's concept of diadochism of In^{3+} to Fe^{2+} and Mg^{2+} was simply based on the theory of ionic radii, from which In^{3+} replacement of Fe^{3+} in solid solution appeared improbable, because of the large difference of ionic radii given by Goldschmidt (1927) (Fe^{3+} 0.67 Å In^{3+} 0.92 Å). Shaw's spectrographic analyses could be more easily interpreted as isomorphous substitution than diadochism. Theories such as sulfide inclusions, surface absorption, indium province or mechanical impurity should be excluded in the absence of direct evidence.

The behavior of In^{3+} in sedimentary processes may be similar to that of Sc^{3+}, Fe^{3+} and possibly Al^{3+}. In fact, indium was occasionally detected in small amounts in the sedimentary iron ores and bauxite deposits. It seems probable that indium ore will be formed in the vicinity of large iron deposits by fractional precipitation. Such a phenomenon was found at Fairfield, Utah (Frondel, Ito and Montgomery, 1968) for scandium deposits among aluminum phosphate deposits, because $AlPO_4 \cdot 2H_2O$, $FePO_4 \cdot 2H_2O$, $ScPO_4 \cdot 2H_2O$ and $InPO_4 \cdot 2H_2O$ are proved to be isostructural and stable under the same conditions (Borenstajin, 1966).

REFERENCES

BORENSTAJIN, J. (1966) Structures cristallines de la metavariscite et de la metastrengite. *Bull. Soc. Franç. Minéral. Cristallogr.*, **89**, 428–438.

BROOKS, R. R., AND L. H. AHRENS (1961) The determination of indium and thallium in G-1, W-1 and other silicate rocks by a new technique. *Geochim. Cosmochim. Acta*, **23**, 145–147.

CHRISTENSEN, A. N., AND R. C. HAZEL (1967) The crystal structure of $NaIn(SiO_3)_2$. *Acta Chim. Scand.*, **21**, 1425–1429.

ERÄMAETSÄ, O. (1938) The distribution of indium in Finnish minerals and its separation from other minerals. *Ann. Acad. Sci. Fennicae*, **A 51**(1), 1–92.

FRONDEL, C., AND J. ITO (1968) Synthesis of the scandium analogue of beryl. *Amer. Mineral.*, **53**, 943–953.

——— AND——— (1967) Crystal chemistry and geochemistry of scandium. *Int. meet. GAC, MAC, MSA, AZOPORO, Kingston, Ont., Can., Abstr. 27.*

———, ———, and A. MONTGOMERY (1968) Scandium content in some aluminum phosphates. *Amer. Mineral.*, **53**, 1223–1231.

GELLER, S., H. J. WILLIAMS AND R. C. SHERWOOD (1961) Substitution of Fe^{3+} ion in Sc_2O_3 and In_2O_3. *J. Chem. Phys.*, **35**, 1908–1909.

GENKIN, A. D., AND I. V. MURAVEVA (1958) Indite and dzhalinite, a new indium mineral. *Zap. Vses. Mineral. Obshch.* **92**, 445–457.

GOLDSCHMIDT, V. M. (1937) The principles of the geochemical distribution of the elements. (IX) The abundance of the elements and isotopes. *Skr. Norske Vidensk. Akad. Oslo, I. Mat. Naturv. No.* **4**, 1–148.

ITO, J., AND C. FRONDEL (1967) Syntheses of the kentrolite-melanotekite series. *Arkiv Mineral. Geol.*, **4**, 387–390.

——— AND ——— (1968) Syntheses of the scandium analogues of aegirine, spodumene, andradite and melanotekite *Amer. Mineral.*, **53**, 1276–1280.

——— AND H. JOHNSON (1968) Synthesis and study of yttrialite. *Amer. Mineral.*, **53**,, (in press).

IVANOV, V. V. (1963) Indium in some igneous rocks of the USSR. *Geokhimiya* **1963**, 1101–1110 [Transl. *Geochemistry*, **1963**, 1150–1160]

KATO, A. (1965) Sakuraiite, a new mineral. *Chigaku Kenkyn*, **Sakurai Special Vol.**, 1–5 (In Japanese).

KEITH, M. L., AND R. ROY (1954) Structural relations among double oxides of trivalent elements. *Amer. Mineral.*, **39**, 1–23.

MAGUIRE, E. A., AND J. J. GREEN (1967) Magnetic properties of yttrium, gadolinium, iron, aluminum and indium garnets. *J. Amer. Ceram. Soc.*, **50**(4), 208–210.

MILL, B. V. (1964) Hydrothermal synthesis of garnets containing V^{3+}, In^{3+} and Sc^{3+}. *Doklad. Akad. Nauk USSR*, **156**, 814–816.

PAULING, L. (1960) *The nature of the chemical bond. 3rd ed.*, Cornell Univ. Press, Ithaca, N. Y., p. 514.

PICOT, P., AND R. PIERROT (1963) Roquesite, a new mineral. *Bull. Soc. Franç. Minéral Cristallogr.*, **86**, 7–14.

RANKAMA, K., AND TH. G. SAHAMA (1950) *Geochemistry.* Univ. Chicago Press, Chicago, Ill., p. 125.

ROTH, R. S., AND S. J. SCHNEIDER (1960) Phase equilibria in system involving the rare earth oxides: 1. Polymorphism of the oxides of trivalent rare earth ions. *J. Res., Nat. Bur. Stand. (U.S.)* **64A**, 309–316.

SHANNON, R. D. (1966) New high pressure phases having the corundum structure. *Solid State Comm.* **4**, 629–630.

SHAW, D. M. (1952) The geochemistry of indium *Geochim. Cosmochim. Acta*, **2**, 185–206.

SCHNEIDER, S. J., R. S. ROTH AND J. L. WARING (1961) Solid state reactions involving oxides of trivalent cations. *J. Res., Nat. Bur. Stand. (U.S.)*, **65A**, 345–374.

TEMPLETON, D. H., AND C. H. DAUBEN (1954) Lattice parameters of some rare earth compounds and a set of crystal radii. *J. Amer. Chem. Soc.*, **76**, 5237–5239.

WELLS, A. F. (1962) *Structural inorganic chemistry, 3rd ed.* Oxford, Clarendon Press, p. 483.

SCHWARZ, H. (1967) Neue Verbindungen mit Granatstruktur, II. Hydrogranate, *Z. Naturforschg.*, **22b**, 554–556.

Manuscript received, April 19, 1968; accepted for publication, July 11, 1968.