Mineral chemistry of synchysite from Dhani granite, Pali district, Rajasthan, India

Synchysite-(Ce), CeCaF(CO₃)₂, is a member of the rare earth fluorocarbonate group of minerals, one of the important ore minerals of the rare earth elements (REE)¹. The rare earth fluorocarbonates have considerable interest because of their economic importance. Synchysite-(Ce) was first discovered in syenite pegmatites from Narssarssuk, Greenland². It belongs to the parisite family and can be formed by various geological processes such as magmatic, metasomatic and sedimentary origin as well as in hydrothermal ore deposits³.

The Meso-Proterozoic Erinpura Igneous Suite occurs in southwestern Rajasthan, west of the Aravalli Range. Dhani granite is exposed over 5 sq. km with a linear trend in the NE-SW direction and is a peraluminous porphyritic granitic pluton within Erinpura Igneous Suite (Figure 1). The analytical results of bedrock samples of Dhani granite indicate high anomalous REE value up to 9160 ppm (ref. 4). The REE-bearing mineral phases identified in the Dhani granite sample by electron probe micro analyser (EPMA) are monazite-(Ce), synchysite-(Ce), allanite-(Ce) and xenotime-(Y).

Dhani granite is leucocratic, porphyritic, often fractured, jointed and brecciated. The western contact of Dhani granite and Erinpura granite is faulted and the eastern contact could not be deciphered due to alluvium cover. It is traversed by feebly carbonated ferrugineous chert, pegmatite and quartz veins, and shows intense brecciation, silicification, alteration and epidotization. Mediumgrained granite is a non-porphyritic, biotite-rich younger intrusive phase and is exposed at the contact between Dhani granite and Erinpura granite.

Petrography of Dhani granite indicates that it is composed of orthoclase, microcline and quartz with minor amount of plagioclase and muscovite along with accessory minerals such as zircon, sphene, apatite and opaque. Feldspar (orthoclase, microcline and plagioclase) grains are often highly altered. Sericitization and kaolinization of plagioclase are common and developed along the twin lamellae, cleavage and fracture planes. Quartz grains are mostly deformed and show deformed lamellae, undulose extinction and suture grain boundary. Perthetic and graphic texture are most common in Dhani granite.

Dhani granite is peraluminous, as corroborated by the presence of muscovite and normative corundum. It is potassic and highly siliceous, and can be designated as S-type granite⁵. The Dhani granite has anomalously higher enrichment of LREE than HREE. High Rb/Sr and Ba/Sr ratios, high K content and relative enrichment of high-field-strength elements suggest that Dhani granite is derived from a felsic source characterized by high potassium and low calcium content. Chondrite normalized pattern of REE of Dhani granite shows negative Eu anomaly, indicating early separation of plagioclase in Dhani granite.

Electron microprobe analysis of different samples of Dhani granite was carried out at the EPMA Laboratory, Geological Survey of India, Faridabad using CAMECA SX-100 instrument. For the analysis, various surface and core samples from the mineralized zone were collected and a thin polished section was prepared. The analytical condition for REE was maintained through accelerating voltage of 20 kV and 30 nA current with peak counting time of 30 sec for all elements. Beam size for the analysis was 1 μ m. All the natural standards were used for calibration of the instrument.

In the EPMA study, a total of 30 points were analysed for synchysite from selective samples of REE-mineralized zones of Dhani granite. Mainly three types of synchysite were observed - synchysite-(Ce), synchysite-(Nd) and synchysite-(Y). Synchysite grains of Dhani granite show that Ce₂O₃ varies from 20.49 to 25.70 wt%, Nd₂O₃ from 8.42 to 10.59 wt%, La₂O₃ from 10.26 to 13.87 wt%, CaO from 15.89 to 18.21 wt%, and F from 3.60 to 6.97 wt% (Table 1). The total weight percentage of each synchysite grain is low due to presence of volatiles (CO₂, H₂O, etc.). In general, CO₂ wt% in synchysite varies from 27 to 30. Studies on synchysite worldwide^{3,6,7} have shown



Figure 1. Geological map of Dhani area, Pali district, Rajasthan.

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Sample	24-DGBH-3		26-D	GBH-3	D	G11	60A-DGBH-3	
Dataset/point	4/1	10/1	2/1	4/1	1/1	6/1	2/1	4/1
P ₂ O ₅	0.031	0.012	0.012	0.033	0.011	0.302	0.013	0.000
Y_2O_3	1.795	1.014	1.150	0.733	1.021	2.032	1.622	1.381
La_2O_3	11.549	12.600	11.090	11.840	11.015	10.603	12.977	13.872
PbO	0.011	0.000	0.034	0.000	0.016	0.019	0.000	0.000
UO ₂	0.001	0.000	0.000	0.000	0.070	0.000	0.000	0.011
Ce_2O_3	23.453	23.145	22.691	22.465	24.139	24.088	24.965	25.701
Nd_2O_3	8.423	10.048	10.249	9.878	10.046	10.347	9.740	9.764
SiO ₂	0.168	0.094	0.027	0.078	0.690	1.065	0.090	0.060
ThO ₂	0.125	0.332	0.000	0.009	0.576	0.686	0.000	0.000
K ₂ O	0.003	0.003	0.012	0.016	0.076	0.000	0.000	0.000
CaO	17.873	15.899	17.897	18.205	17.048	16.123	17.383	16.095
Pr ₂ O ₃	2.887	3.319	3.304	3.078	3.373	2.843	2.950	2.938
Sm_2O_3	1.704	2.190	1.964	1.932	2.163	1.963	1.853	1.914
Gd_2O_3	1.285	1.440	0.866	1.217	0.998	1.485	1.109	1.143
Dy ₂ O ₃	0.555	0.341	0.624	0.236	0.414	0.614	0.427	0.169
F	4.157	4.426	3.641	3.850	6.996	4.508	4.594	5.344
Total	74.023	74.864	73.560	73.570	78.652	76.678	77.723	78.392
Р	0.007	0.003	0.003	0.007	0.002	0.061	0.003	0.000
Y	0.238	0.138	0.154	0.098	0.133	0.259	0.209	0.181
La	1.062	1.186	1.028	1.096	0.992	0.936	1.161	1.262
Pb	0.001	0.000	0.002	0.000	0.001	0.001	0.000	0.000
U	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.001
Ce	2.141	2.163	2.088	2.063	2.158	2.110	2.216	2.320
Nd	0.750	0.916	0.920	0.885	0.876	0.884	0.844	0.860
Si	0.042	0.024	0.007	0.020	0.169	0.255	0.022	0.015
Th	0.007	0.019	0.000	0.001	0.032	0.037	0.000	0.000
K	0.001	0.001	0.004	0.005	0.024	0.000	0.000	0.000
Ca	4.775	4.348	4.819	4.894	4.461	4.134	4.516	4.253
Pr	0.262	0.309	0.303	0.281	0.300	0.248	0.261	0.264
Sm	0.135	0.177	0.157	0.154	0.168	0.149	0.143	0.150
Gd	0.106	0.122	0.072	0.101	0.081	0.118	0.089	0.093
Dv	0.045	0.028	0.051	0.019	0.033	0.047	0.033	0.013

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Table 1. Mineral chemistry (oxide wt% and cation analysis) of synchysite grains from Dhani granite, Pali district, Rajasthan

Table 2. Study of synchysite mineral composition of Dhani granite samples and those worldwide

Area	Dhani area, Pali, Rajasthan Synchysite (n = 30) Porphyritic granite			Tundlu Complex, Malawi ⁶ Carbonatite		Reyan basaltic amygdules, Esterel volcanic rock, France ⁷ Basaltic amygdules		Variscan granites of the German Erzgebrige, Germany ³ Monzogranite	
Sample									
Rock type									
Dataset/point	Minimum	Maximum	Average	G1332/1	G1332/2	1	6	GOT, Gb-71/7	ZNW, SF-1149-FS/8
P ₂ O ₅	0.000	0.302	0.029	_	_	_	_	_	_
Y_2O_3	0.733	2.032	1.223	_	_	0.000	0.000	0.940	2.630
La_2O_3	10.262	13.872	11.467	13.300	16.900	14.090	13.780	11.800	5.200
PbO	0.000	0.037	0.008	_	_	_	_	0.000	0.300
UO_2	0.000	0.083	0.011	0.000	0.007	0.000	0.000	0.000	0.050
Ce_2O_3	20.494	25.701	23.035	26.900	28.400	24.040	25.270	25.600	24.000
Nd_2O_3	8.423	10.594	9.674	8.210	6.090	9.880	9.570	9.900	11.900
SiO ₂	0.027	2.793	0.408	1.550	0.310	_	_	0.160	0.430
ThO ₂	0.000	0.686	0.185	1.600	0.360	0.000	0.000	0.000	1.100
K ₂ O	0.000	0.299	0.038	_	_	_	_	-	-
CaO	15.899	18.205	17.487	14.700	15.900	18.090	18.330	17.200	16.600
Pr ₂ O ₃	2.711	3.452	3.039	2.140	2.220	2.300	2.250	2.610	3.060
Sm_2O_3	1.208	2.250	1.858	0.690	0.230	1.070	1.040	2.300	2.760
Gd_2O_3	0.817	1.977	1.218	0.500	0.180	0.470	0.390	1.490	1.210
Dy_2O_3	0.152	0.624	0.375	_	-	0.000	0.000	0.230	0.510
F	3.604	6.996	4.305	3.060	3.090	6.590	6.030	5.620	5.170

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Figure 2. Back-scattered electron images of mineral phases identified in Dhani granite. a, Anhedral synchysite in association with monazite occurring between the grain boundary of alkali feldspar and quartz. b, Subhedral to anhedral discrete grains of synchysite as an inclusion within quartz. c, Subhedral to anhedral discrete grains of synchysite and monazite, where synchysite replaces monazite. d, Anhedral grains of synchysite trap sericite flakes in Dhani granite sample.

that the wt% of Ce₂O₃ varies from 24.00 to 28.40, Nd₂O₃ from 6.09 to 11.90, La₂O₃ from 5.20 to 16.90, CaO from 14.70 to 18.33, and F from 3.06 to 6.59. Similar range of average wt% of REE oxides of synchysite were noted in Dhani granite samples (Table 2). Chemical analysis of synchysite from Dhani granite indicates that it is mostly synchysite-(Ce) variety. Synchysite grains are mostly associated with monazite, rutile, ziron and apatite. The synchysite mineral phases are in general subhedral to anhedral in shape and have size ranging from 25 to 500 µm. They occur as discrete grains along the grain boundaries of alkali feldspar-quartz and as inclusions within quartz and alkali feldspar (Figure 2 a-c). Synchysite grains are found to trap sericite and chlorite grains (Figure 2 d). This implies that synchysite grains are formed later than the altered sericite and chlorite grains. The textural relationship of synchysite with other associated mineral phases indicates that it forms from late-phase fluid activity and alteration. The other REE-bearing phases identified in Dhani granite samples are monazite $((REE, Th)PO_4),$ allanite ((Ca, REE,Al,Fe)SiO₄·H₂O) and thorite (ThSiO₄) grains. Their association, i.e. textural relationship and mineral assemblages indicate that thorite and synchysite are the products of monazite alteration and reaction with fluorine- and calcium-rich hydrothermal fluid. This fluid also alters the feldspar grains, thus leading to the formation of sericite and chlorite which are trapped within the newly formed synchysite grain. Thorium of monazite grains is mobile and forms thorite mineral with excess silica-rich fluid within the system. Synchysite is interpreted as being derived from the dissolution of monazite during interaction with an F-CO₂-Ca-bearing fluid, its composition reflecting the differential mobility of LREE and thorium during fluid-rock interaction. A late stage of hydrothermal alteration is characterized by calcite ± fluorite assemblages observed in replacements of albitized feldspar and chloritization within the Dhani granite. Petrographic study of Dhani granite shows complete association of albitized, chloritized and kaolinized feldspar with calcite and REE-bearing flurocarbonates such as synchysite. Formation of synchysite being a late hydrothermal process within the Dhani granite is supported by

the presence of calcite-altered feldspar association, trapping of sericite-chlorite flakes within the newly formed synchysite grains and association of monazite-thorite with synchysite grains.

The main REE bearing mineral phases of Dhani granite are synchysite, monazite and xenotime. Detailed EPMA and petrography studies of Dhani granite indicate that the REE mineralization and formation of synchysite in Dhnai granite are due to hydrothermal process.

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