NOTE

Natroalunite on Ruapehu volcano, New Zealand

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A 5cm diameter nodule recently recovered from the northern slopes of Mount Ruapehu, Taupo Volcanic Zone, New Zealand consists of bladed natroalunite, quartz and rutile. The natroalunite crystals are zoned, having K-rich cores and Na-rich rims, and are enriched in Ba and Sr over Rb. The strontium isotopic composition (0.70535) is close to the average for Ruapehu lavas and the $\delta^{34}\text{S}$ (‰) CDT value of +16.1 is similar to dissolved sulphate in Ruapehu crater lake. The nodule probably originated as a precipitate from hydrothermal fluids at low pH, and was subsequently baked by hot lava.

INTRODUCTION

The precipitation of alunite from hot waters is commonly observed in geothermal and fumarolic areas of active volcanism around the world, e.g., Raymahashay (1968). In New Zealand, alunite minerals have been reported from the Wairakei geothermal area (Steiner, 1953) and the volcanoes: Mt. Egmont (Wood, 1971), White Island (Slansky, 1975) and Mt. Ruapehu crater lake (Giggenbach, 1974). The example described here (Victoria University catalogue No. 17426) is unusual because it was recovered as a small (5cm diameter) float-block nodule in the Whakapapanui stream bed, northern Ruapehu. Though of uncertain derivation it was most probably an inclusion in a recent Whakapapa Formation flow (W. R. Hackett, pers. comm. 1984). This note reports the chemistry and isotopic compositions of the nodule and its origin is discussed.

MINERALOGY, CHEMISTRY AND ISOTOPIC COMPOSITION OF THE NODULE

Mineralogy

The nodule is speckled orange-brown, is well-indurated and has a light-brown rind enclosing a fresh interior. Microscopic examination reveals a simple mineralogy of 0.1 to

0.2mm granular quartz grains (45%), fibrous, sometimes radiating clots of natroalunite (55%) and traces of rutile (Fig. 1). Individual natroalunite crystals are less than 0.5mm wide and only a few microns thick. XRD analysis of the bulk-rock confirmed this mineralogy (see Table 1); all but two minor, high-angle peaks were assigned to either natroalunite, quartz or rutile and these are considered to be previously unreported peaks belonging to natroalunite.

Chemistry

Bulk rock chemistry is shown in Table 2; analytical methods used are those given in Graham (1985a). The sulphur content of the bulk rock was determined as 8.8% by HF/HNO₃/H₃BO₃ digestion and precipitation/weighing of the sulphate as BaSO₄. Low concentrations of Fe₂O₃, MnO, MgO and CaO result from quartz, natroalunite and rutile containing only trace amounts of these elements. In the bulk nodule the only trace elements attributable to the natroalunite phase at concentrations ≥ 10 mg/kg are: Ba (114mg/kg), Sr (134mg/kg) and Rb (10mg/kg).

Ignition losses confirm the DTA patterns reported previously for natroalunite (Kashkai and Babaev, 1969) and indicate dewatering at 400-500°C and partial thermal decomposition (2/3 S loss) at 700-900°C. EPMA analysis of

the natroalunite crystals was extremely difficult owing to their high water content and thinness. Nevertheless, a partial analysis (Table 2) is similar to that derived after recalculating the bulk-rock analysis by removing from it SiO₂ (quartz) and TiO₂ (rutile). Individual natroalunite crystals are zoned (Fig. 1) with an increase in Na in the rims but constant S and Al contents.

Isotopic Composition

The whole rock ⁸⁷Sr/⁸⁶Sr ratio of the nodule is 0.70535 ± 0.00005 and the Sr is assumed to be present only in natroalunite. Natroalunite was leached from the nodule and the dissolved sulphate precipitated as BaSO₄ for sulphur isotopic analysis. Its δ³⁴S_{CDT} value is +16.1 ± 0.2‰.

Fig. 1. Back-scatter Electron Image photograph of natroalunite-bearing nodule VUW 17426. Natroalunite blades are zoned with Na_{0.57} cores (lighter) and Na_{0.75} rims (darker). Other minerals are quartz (light-grey) and rutile (white). Scale bar (bottom right) = 0.1 mm (100 μm).

Table 1. X-ray powder diffraction data of natroalunite in VUW 17426, compared to data published by Slansky (1975) (WI-4) and Parker (1962)

17426		WI-4		Parker	
dÅ	I	dÅ	I	dÅ	I
5.693	25	5.688	17	5.69	12
5.610	14	—	—	5.58	12
4.918	>100	4.905	64	4.90	75
3.490	50	3.488	32	3.49	24
2.966	>100	2.973	100	2.97	70
2.965	>100	2.966	89	2.96	100
2.789	14	—	—	2.79	18
2.222	41	2.224	11	2.221	50
2.203	16	2.208	6	2.202	12
1.894	54	1.896	22	1.894	30
1.858	8	—	—	1.857	10
1.741	39	1.744	17	1.744	22
1.641	9	1.644	2	1.643	6
1.500	7	1.501	2	1.501	6
1.463	17	—	—	1.463	12
1.316	5	—	—	—	—
1.282	13	—	—	—	—

NOTES: CuKα radiation; Ni filter.

DISCUSSION

Slansky (1975) reported an occurrence of natroalunite on White Island volcano: sample WI-4 appeared as a chalky-white, fine grained fragment with petrographic features similar to altered andesitic lava. Similarly, Raymahashay (1968) described the alteration of rhyolites by acid-sulphate springs to an assemblage of kaolinite, alunite and silica minerals, a process which has been demonstrated experimentally (Höller, 1967). For the Mt. Ruapehu volcano, Giggenbach (1974) described the suspended sediment material in the crater lake as consisting of amorphous silica, cristobalite, sodic alunite, gypsum and unaltered andesitic particles.

The composition of the alunite analysed by Giggenbach (1974) is Na_{0.56}K_{0.44} which corresponds to that expected for waters with a Na/K atomic ratio of 15 to 20 (Parker, 1962; Zotov, 1971). Considering the exchange reaction:

Hladky and Slansky (1981) show that log $a_{\text{K}^+} / a_{\text{Na}^+} = -5.14$ at 25°C (hence alunite forms

Table 2. Chemistry of natroalunite-bearing nodule 17426

	Bulk rock	Na-alunite 1*	Na-alunite 2*	Rutile	Recalculated Na-alunite**
SiO ₂	44.09	0.00	0.00	0.59	0.00
TiO ₂	0.44	0.00	0.00	95.09	0.00
Al ₂ O ₃	20.99	36.70	37.31	0.30	38.09
FeO	0.21	0.00	0.00	3.21	0.00
MnO	0.00	0.00	0.00	0.00	0.00
MgO	0.02	0.00	0.00	0.00	0.00
CaO	0.09	0.00	0.00	0.00	0.00
Na ₂ O	2.98	4.70	6.02	0.00	5.41
K ₂ O	1.52	4.80	2.66	0.00	2.76
P ₂ O ₅	0.04	0.00	0.00	0.00	0.00
Cr ₂ O ₃	0.02	0.00	0.00	0.88	0.00
SO ₃	26.29***	37.40	37.40	0.00	39.95
H ₂ O		—	—	0.00	13.79
Total	96.69	83.59	83.39	100.07	100.00

* EPMA analyses of natroalunite core (Na-alunite 1) and rim (Na-alunite 2) with beam width of 10 µm and reduced current. These analyses do not include water.

** Natroalunite recalculated assuming only Al, Na, K, S and water included.

*** Loss on ignition at 1,000°C represents total combined H₂O and 2/3 equivalent SO₃.

under most normal conditions) but the minerals can theoretically coexist for pH < 4. Zotov (1971) analysed alunites and coexisting thermal waters (up to 82°C) and concluded that, for weakly mineralised, moderately acid solutions, the equilibrium for reaction (1) lies towards enrichment in K for alunites formed at higher temperatures. However, in more concentrated solutions the mineral composition will depend not only on temperature but on pH and Zotov (1971) found that in the Ebeko volcanic springs with pH 0.5 and mineralisation up to 20g/kg Na-alunite forms. Similarly for the Ruapehu crater lake with mineralisation 28g/kg and pH 1.3 natroalunite would be expected and the natroalunite in the nodule has Na_{0.57-0.75}. The mineral is thought to have been formed from a solution whose dissolved constituents were leached from andesitic magma.

The average Ruapehu andesite contains : 3% Na, 1.5% K, 250mg/kg Sr, 350mg/kg Ba and 50mg/kg Rb. Crater lake waters contain 800-1,500mg/kg Na, 80-200mg/kg K, 1-3mg/kg Sr and 0.4-2.2mg/kg Rb (Giggenbach, 1974). Significant amounts of Sr (134mg/kg) and Ba (114mg/kg) enter the natroalunite (and probably also gypsum). The K-Na site in alunite has 12 fold co-ordination and is relatively tolerant to ionic size. Sr and Ba are reasonably

close to K and Na in size and are, in addition, doubly charged. However, Rb with a significantly larger ionic radius and only a single charge is not admitted to the structure and concentrates in the solution.

The zonation of the alunite crystals as shown in Fig. 1 with Na richer rims must be explained. Giggenbach (1974) reported a detailed study of the Mt. Ruapehu Crater Lake chemistry covering before, during, and after an eruptive period in 1971. The lake water is saturated or supersaturated with many constituents derived from the interaction of acid waters with andesitic magma. Increases in the concentration of elements such as Na (which are not limited by solubility) were noted during the eruptive period and during quiet periods the concentration decreases owing to dilution by meteoric and fumarolic water. The concentrations of sulphate, Ca, Al, K (and to a small extent Na) are controlled by the precipitation of gypsum and alunite in response to variations in the sulphate concentrations as a result of changes in pH, according to:

During an eruptive period acid gases are absorbed by the lake water and remain in solu-

tion but Giggenbach (1974) shows that these acids are partly neutralised by the oxidic constituents of the magma so that the pH of the lake water increases during such a period (from 1.2 to 1.8) and then drops again to 1.2. Over the same period the sulphate concentration dropped from about 10,900 mg/kg to 500 mg/kg then rose to 16,800 mg/kg. Similarly Na and K rose from 750 and 80 mg/kg to 1,500 and 100 mg/kg respectively, thereafter Na decreased to 1,100 mg/kg and K increased to 200 mg/kg (Giggenbach, 1974). The drop in sulphate represents the precipitation of gypsum and alunite but the later steady increase in sulphate and K result from the redissolution of these minerals as a function of the decrease in pH. Lake sediment samples analysed by Giggenbach (1974) show an enrichment of Na during the eruptive period and could account for the natroalunite crystal-cores with $\text{Na}_{0.57}$. The natroalunite crystal-rims with $\text{Na}_{0.75}$ presumably formed during an even more active period in the lake when the Na/K ratio in the water was higher. The zoning then represents two active periods in the lake, the last one being more active with a probable dissolution period in between.

Dissolved sulphate in the crater lake has been analysed for its sulphur isotopic composition since 1968. The average $\delta^{34}\text{S}_{\text{CDT}}$ is $+17.8 \pm 1.1\text{‰}$ ($n = 12$). Elemental sulphur in the lake has a $\delta^{34}\text{S}$ value of about -7.9‰ and a sample of gypsum a value of $+13.5\text{‰}$. Sulphate forms in the lake by oxidation of H_2S and SO_2 gas. Isotopic fractionation between this sulphate and the reduced sulphur will take place because of the low pH and high SO_4 concentration ($\sim 10,600$ mg/kg), although equilibrium values have not been reached. The $\delta^{34}\text{S}$ value for the natroalunite nodule ($+16.1\text{‰}$) links it to the crater lake or similar environment at a time when the dissolved sulphate had a slightly lower $\delta^{34}\text{S}$ value. The measured Sr isotopic composition of the natroalunite (nodule) is close to the average of 101 analyses of Ruapehu lava: $^{87}\text{Sr}/^{86}\text{Sr} = 0.70531 \pm 0.00062$ (2σ) (Graham, 1985b).

Natroalunite, quartz, and rutile were precipitated in hydrothermal waters emanating from Mt. Ruapehu or in the crater lake. This explains best the simple mineralogy and bulk rock chemistry of the nodule. The indurated nature of the inclusion resulted from the thermal effect of contact with hot lava during eruption but the nodule could not have been a xenolith as such, since combined water would have been lost from the natroalunite at temperatures above 400°C . It is surprising that rutile and not anatase (the TiO_2 polymorph normally found in the hydrothermal environment) is formed. Since it is not known from the lavas of Mt. Ruapehu, it can not be a residual mineral from andesite decomposition.

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