

SECONDARY SILICIFICATION OF RHYOLITES FROM THE FOCAL PEAK SHIELD VOLCANO, AUSTRALIA

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ABSTRACT

This paper describes some of the compositional changes accompanying secondary silicification of some rhyolites from the Mt Gillies Volcanics, southeastern Queensland, Australia. It is believed that the relatively high SiO_2 content (up to 81.83%) of the silicified rhyolites is due to the preferential loss of the majority of other oxides from the rhyolites. Models are presented to explain this behaviour.

INTRODUCTION

IN southeastern Queensland and northeastern New South Wales, Australia, the extinct Focal Peak Shield Volcano exists^{1,2}. The eruptives of the volcano are late Oligocene in age and include the Mt Gillies Volcanics.

The rhyolites of the Mt Gillies Volcanics are composed of numerous eruptives and dykes and an occasional plug. The rhyolites are metaluminous³ in composition and consist of pitchstones as well as non-glassy rhyolites. The present discussion is concerned with the secondary silicification observed in some of the non-glassy rhyolites.

MINERALOGY OF RHYOLITES OF THE MT GILLIES VOLCANICS

A knowledge of the phenocrystic mineralogy of the rhyolites is important in understanding the mechanism of silicification and the accompanying changes in the whole rock chemical composition.

Phenocrystic phases within the rhyolites are sanidine (and minor anorthoclase) +/- quartz +/- ferrohedenbergite (and minor ferroaugite) + fayalite + ilmenite +/- ferrohypersthene + zircon + chevkinite +/- ferropigeonite +/- partially resorbed plagioclase in the order of decreasing abundance. Pyroxenes, fayalite and ilmenite in the non-glassy rhyolites are nearly always altered to chlorite, haematite and maghemite; such alteration is less common in the pitchstones.

GEOCHEMICAL CHANGES ACCOMPANYING SILICIFICATION

The processes of devitrification and silicification cannot be separately identified within the rhyolites and

hence the two are considered as one process here. Field, mineralogical and, to a lesser extent, geochemical data on the pitchstones and non-glassy rhyolites indicate that they had similar geochemical compositions prior to silicification and devitrification.

To compare the chemical compositions of the pitchstones and the non-glassy rhyolites all analyses were recalculated on the basis of loss on ignition being zero, all iron expressed as FeO and normalization to 100% for the oxides. The pitchstones and non-glassy rhyolites average respectively 3.58 and 0.98% for the loss on ignition. All iron was calculated as FeO partly because we are interested in changes in iron content during silicification. Trace elements were not recalculated as the data would have changed only slightly e.g. Rb would change from say 150 to 155 ppm and Ni would remain unchanged at 7 ppm.

In table 1 averages of pitchstones, non-glassy rhyolites, the most silicified non-glassy rhyolites, and matrices from the pitchstones and the non-glassy rhyolites are presented. Unbiased standard deviations for all averages and three analyses of the silicified non-glassy rhyolites are also presented.

The SiO_2 contents of the recalculated analyses of non-glassy rhyolites range from 74.59 to 81.83% (average 79.14%) whereas the range for the pitchstones is 75.33 to 78.97% (average 76.31%) (see table 1). Enrichment in SiO_2 therefore occurred in some non-glassy rhyolites.

Alumina (Al_2O_3), total iron expressed as FeO, CaO, Ba, Sr and Zn are notably depleted in silicified non-glassy rhyolites (see table 1). TiO_2 , MgO, K_2O , Zr and rare earth elements are depleted to a lesser degree. The majority of the remaining oxides and trace elements are relatively unchanged during silicification. (However the limited data for quartzo-feldspathic matrices from non-glassy rhyolites suggest that during

Table 1 Compositions of pitchstones and non-glassy rhyolites from the Mt Gillies Volcanics, southeast Queensland

	Non-glassy rhyolites:			Matrices from		Examples of silicified rhyolites		
	Pitchstones Av. S.D. N=18*	"Most" Silicified: Av. S.D. N=7*	All Av S.D. N=19*	Pitchstones Av. S.D. N=11*	Non-glassy Rhyolites Av. S.D. N=6*	Sample 1	Sample 2	Sample 4
(wt %)								
SiO ₂	76.31 ± 0.81	80.90 ± 0.51	79.14 ± 1.84	76.71 ± 0.63	79.19 ± 2.67	80.21	80.35	81.83
TiO ₂	0.18 ± 0.04	0.11 ± 0.02	0.13 ± 0.04	0.14 ± 0.03	0.10 ± 0.02	0.11	0.14	0.12
Al ₂ O ₃	12.41 ± 0.26	10.08 ± 0.47	11.18 ± 1.12	12.28 ± 0.45	11.36 ± 1.61	9.81	10.69	9.64
FeO	1.61 ± 0.36	0.82 ± 0.30	0.90 ± 0.42	1.58 ± 0.18	0.76 ± 0.20	1.52	0.63	0.67
MnO	0.03 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.02 ± 0.02	0.02	0.01	0.01
MgO	0.27 ± 0.40	0.18 ± 0.20	0.12 ± 0.16	0.03 ± 0.05	0.06 ± 0.07	0.66	0.13	0.14
CaO	0.62 ± 0.23	0.31 ± 0.09	0.33 ± 0.11	0.60 ± 0.13	0.28 ± 0.08	0.35	0.40	0.33
Na ₂ O	3.10 ± 0.46	3.14 ± 0.72	3.31 ± 0.56	3.08 ± 0.41	3.19 ± 0.74	2.92	3.05	2.26
K ₂ O	5.47 ± 0.43	4.44 ± 0.32	4.86 ± 0.45	5.56 ± 0.38	5.02 ± 0.29	4.39	4.57	4.99
P ₂ O ₅	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.01	0.01	0.01
(ppm)								
Rb	153 ± 10	150 ± 15	159 ± 20	185 ± 16	139 ± 30	139	149	142
Sr	11.2 ± 8.8	5.6 ± 2.9	6.5 ± 4.4	6.3 ± 7.5	2.8 ± 2.2	4	8	n.d.
Ba	97 ± 36	51 ± 23	61 ± 29	56 ± 21	46 ± 21	46	60	57
Pb	22 ± 3.3	20 ± 3.9	21 ± 3.9	27 ± 2.6	29 ± 5.2	17	20	26
Th	20 ± 1.4	18 ± 1.8	20 ± 2.2	24 ± 2.5	20 ± 3.4	18	19	18
Zr	346 ± 27	269 ± 32	316 ± 64	294 ± 32	207 ± 83	279	311	267
Nb	35 ± 3.1	38 ± 12	41 ± 13	39 ± 6	37 ± 15	32	31	31
La	78 ± 13	54 ± 26	62 ± 31	87 ± 13	60 ± 22	34	69	26
Ce	174 ± 23	127 ± 51	142 ± 63	180 ± 17	134 ± 53	73	150	91
Nd	86 ± 15	66 ± 24	72 ± 33	92 ± 12	69 ± 26	39	77	46
Y	75 ± 11	68 ± 40	72 ± 48	83 ± 9	46 ± 25	33	66	27
V	19 ± 2.0	1.3 ± 1.3	1.5 ± 1.4	2.8 ± 1.7	3.8 ± 1.0	4	2	1
Cr	1.5 ± 1.3	1.7 ± 1.7	1.5 ± 1.5	2.3 ± 1.9	1.3 ± 1.3	n.a.	n.a.	n.a.
Co	0.8 ± 0.7	n.a.	1.0	1.6 ± 0.8	n.a.	n.a.	n.a.	n.a.
Ni	6.8 ± 1.4	7.0 ± 1.3	6.7 ± 1.5	4.4 ± 2.3	7.3 ± 2.6	7	7	6
Cu	8.9 ± 2.0	10.4 ± 1.8	10.1 ± 4.5	7.4 ± 4.3	8.8 ± 4.9	11	10	7
Zn	143 ± 17	93 ± 5.3	99 ± 27	163 ± 18	100 ± 31	93	88	91
K/Rb	297	246	254	249	300	262	255	292
PI	0.889	0.990	0.959	0.904	0.942	0.975	0.933	0.948

* number of analyses (N) is as shown for each column excepting: for pitchstones, 13 for Cr, 6 for Co, 16 for Ni; for "most" silicified non-glassy rhyolites, 3 for Cr, 0 for Co; for all non-glassy rhyolites, 14 for Cr, 2 for Co, 18 for Ni; for glassy matrices from pitchstones, 9 for Cr, 5 for Co, 10 for Cu; and for matrices from non-glassy rhyolites, 5 for La, 5 for V, 3 for Cr, 0 for Co, 5 for Cu. P.I. = peralkalinity index (i.e. molar (Na₂O + K₂O)/Al₂O₃); n.a. = not analysed; n.d. = not detected and assumed to be zero in calculations of averages and unbiased standard deviations; Av = average; S.D. = unbiased standard deviation. Method of analysis: xrf for all except flame photometry and atomic absorption for Na₂O. Oxides recalculated to 100% with all iron as FeO.

silicification Rb is depleted.) Few oxides and trace elements (e.g. SiO₂ and possibly Na₂O) are enriched during silicification. The Fe₂O₃/FeO ratio is generally higher for unrecalculated analyses of non-glassy rhyolites (average 2.10) than for unrecalculated analyses of pitchstones (average 0.68).

K/Rb ratios for pitchstones tend to be higher than those of silicified non-glassy rhyolites due to the loss of some K₂O from the latter during silicification (table 1). Data on the matrices from pitchstones and non-glassy

rhyolites reveal that the K/Rb ratio is surprisingly higher in the average non-glassy rhyolitic matrix than in the average glassy matrix—this may be a statistical aberration as only five non-glassy matrices were analysed.

Peralkalinity indices [i.e. molar (Na₂O + K₂O)/Al₂O₃] of rhyolites decrease during silicification, due primarily to the loss of K₂O (see table 1). Such indices need to be interpreted carefully in provinces in which silicification has occurred.

MECHANISM OF SILICIFICATION

An important question, requiring resolution is whether some SiO_2 was added to non glassy rhyolites or whether the other oxides were preferentially (compared to SiO_2) leached out of the non-glassy rhyolites during silicification. If SiO_2 has been added to the non-glassy rhyolites from an external source, the silica veining along fractures and patchy silicification within the non-glassy rhyolites could be expected. These have, however, not been observed. It is therefore believed that the second alternative mentioned above has occurred.

The partial dissolution of phenocrystic phases by H_2O and other volatiles, or chemical alteration of these minerals, means that certain oxides and trace elements are partially liberated from the minerals. The partially liberated oxides and trace elements may be incorporated in the newly formed secondary alteration products (*e.g.* maghemite and chlorite) and/or partially lost from the rhyolites. By studying the pattern of the oxide and trace element losses during silicification, it should be possible to develop some understanding of the mechanism of silicification.

Our first study will concentrate on the loss of Zn during silicification. Nearly all of the ferrohedenbergite (and minor ferroaugite), ferropigeonite, ferrohypersthene, fayalite and ilmenite are completely altered in the non-glassy rhyolites: in the pitchstones, such alteration is less common. The average modal percentages of ferrohedenbergite and fayalite in the pitchstones are 0.7 and 0.2% respectively—the other mafic minerals are each modally less than 0.1%. Ferrohedenbergites from the Mt Gillies Volcanics contain 868–1107 ppm Zn while a fayalite from a green pitchstone belonging to the shield volcano (but not to the Mt Gillies Volcanics) contains 1398 ppm Zn^2 . Based on the alteration of the above mafic mineralogy and modal analyses, the maximum possible loss of Zn from the pitchstones is about 11 ppm. As shown in table 1 the average non-glassy rhyolite loses around 44 ppm Zn during silicification. Glassy matrices lose, however, approximately 63 ppm Zn upon silicification (see table 1) and because the average pitchstone consists of 82.4% glass, then the average pitchstone should lose approximately 52 ppm Zn, a value similar to the observed loss of about 44 ppm. The alteration of glassy matrices therefore contributes most of the observed Zn loss.

Modal analyses show that non-glassy rhyolites contain, on average, slightly less sanidine (11.1%) than the pitchstones (12.7%). The sanidines are com-

posed largely of SiO_2 , Al_2O_3 , K_2O and Na_2O ; and contain 111–479 ppm Ba, 75–89 ppm Rb and 19–58 ppm Sr^2 . If we assume that the difference between the average modal values is due to the partial dissolution of sanidine phenocrysts during silicification, possibly indicated by the rounding of phenocrystic sanidines when viewed under the microscope, then we can expect about 0.31% Al_2O_3 , 0.08% Na_2O , 0.13% K_2O , 5 ppm Ba, 1 ppm Rb, and negligible amounts of other oxides (excluding SiO_2) and trace elements to be lost during silicification. Table 1 shows that about 1.23% Al_2O_3 , 0.61% K_2O and 36 ppm Ba are lost from the average non-glassy rhyolite. On the other hand, Na_2O increases by about 0.21% and Rb stays relatively unchanged during silicification. Table 1 also shows that the average non-glassy rhyolitic matrix, compared to the average matrix from pitchstones, is deficient in Al_2O_3 (0.92%), K_2O (0.54%), Ba (10 ppm) and Rb (46 ppm). The major cause for the loss of Al_2O_3 , K_2O and Ba from silicifying rhyolites therefore appears to be the compositional alteration of the glassy matrices—for Rb the data are contradictory.

At least two models can be conceived to explain the observed compositional changes. The first involves circulation of groundwaters through the rhyolites. Mildly acidic waters (pH ~ 6) encourage the migration of Fe, Mn, Ca, Sr, Ba, Zn, Cr, Ni and Cu whereas the migration of V is enhanced by alkaline waters⁴ (pH > 9). Table 1 shows that iron (expressed as FeO), MnO(?), CaO, Sr, Ba and Zn are lost, but V, Cr, Ni and Cu are relatively unchanged during silicification. This information does not allow one to decide whether or not the groundwaters would indeed be mildly acidic. Neither patchy silicification nor silica deposits along joints are observed and, consequently, the observed silicification may not be due to this model.

The second model involves the reactivity of volatiles, such as H_2O and SO_2 , with matrices and phenocrysts in cooling rhyolites. Reactivity of these volatiles should increase with temperature. Olivine–clinopyroxene and orthopyroxene–clinopyroxene geothermometers give equilibration temperatures of 882–992°C for the pitchstones of the Mt Gillies Volcanics² as compared to rhyolites from other localities such as the Taupo region of New Zealand⁵ (720–915°C), Rabaul Caldera, Papua New Guinea⁶ (890°C), the Mono Craters Rhyolite, California⁷ (800–835°C) and the Topopah Spring Member, Nevada⁸ (720°C). The relatively high temperatures for the Mt. Gillies Volcanics could perhaps have contributed to silicification.

Which of the two models is correct, or whether

another model is required, cannot be ascertained at this stage. The appropriate model will not only have to explain the observed chemical changes, especially for the matrices, but also why some rhyolites, in particular the pitchstones, are unsilicified whereas others show varying degrees of silicification.

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This Workshop organised by Variable Energy Cyclotron Centre, Bhabha Atomic Research Centre, Calcutta is intended to provide an opportunity for an indepth study of the experimental programmes already under way at VEC Centre and discuss the machine hardware and possible future programmes designed to extend the facilities of VEC. Invited speakers will present their programmes, a limited

number of contributed papers based exclusively on experiments performed with VEC will also be presented for oral as well as for poster sessions. This workshop will be held at the VEC Centre, Calcutta on **18-20 February 1986**. For further details please contact Dr. Bikash Sinha, Variable Energy Cyclotron Centre, Bhabha Atomic Research Centre, Sector-I, Block AF, Bidhan Nagar, Calcutta 700 064.
