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ESR dating of quartz phenocrysts in the El Cajete and Battleship Rock Members of Valles Rhyolite, Valles Caldera, New Mexico

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Abstract

The electron spin resonance (ESR) dating method was employed on quartz phenocrysts separated from pumice of the El Cajete and Battleship Rock Members of the Valles Rhyolite in the Valles caldera, New Mexico. The results of heating experiments indicate that Ti impurity centers have two components; a thermally stable one and a less stable, temperature sensitive one. ESR dates using the stable Ti center yield eruption ages of 59 ± 6 ka for the Battleship Rock Member and 53 ± 6 ka for the El Cajete Member while recent ^{14}C dates (S. Reneau and J. Gardner, unpub. data) from carbonized logs in the El Cajete pumice indicate that its age is older than 50 ka. Our results indicate that volcanism in the Valles caldera is much younger than previously thought (≥ 130 ka) and that recent revisions to the post-0.5 Ma stratigraphy of Valles caldera are probably in error. The results suggest that ESR dating of quartz may be a useful method for obtaining ages of units in other Quaternary volcanic areas.

1. Introduction

Quartz is the most common rock forming mineral in the earth's crust and a common constituent in volcanic rocks and hydrothermal deposits; thus methods that can date the crystallization age and thermal history of quartz have tremendous applications in geology, volcanology, and archaeology. Three methods developed in recent years have been successfully used to date quartz (and other minerals): Thermoluminescence (TL), infrared optical (IO), and electron spin resonance (ESR). The three methods are similar in that they measure the concentrations of trapped electrons in defects in crystal structures as functions of time but the theory, instrumentation, and limitations of the methods are different (Aitken, 1985, 1992; Skinner, 1985; Berger, 1988).

The Valles caldera in northern New Mexico (Fig. 1) formed 1.14 Ma and represents the culminating magmatic event of the Jemez volcanic field, which has been continuously active for the last ≥ 13 m.y. (Doell et al., 1968; Gardner et al., 1986; Spell et al., 1990). Valles caldera also contains many post-caldera eruptions of rhyolite domes, flows, and pyroclastic deposits that have been dated by numerous methods most recently summarized by Spell and Harrison (1993).

The ages of the youngest rhyolite lavas and tephras have been the subject of considerable controversy due to stratigraphic complexities in outcrops and drill core, petrologic and geochemical similarities among units, and non-agreement of previous dating results. In fact, recent revisions to the stratigraphy of youngest Valles rhyolites have been perplexingly numerous (Self et al.,

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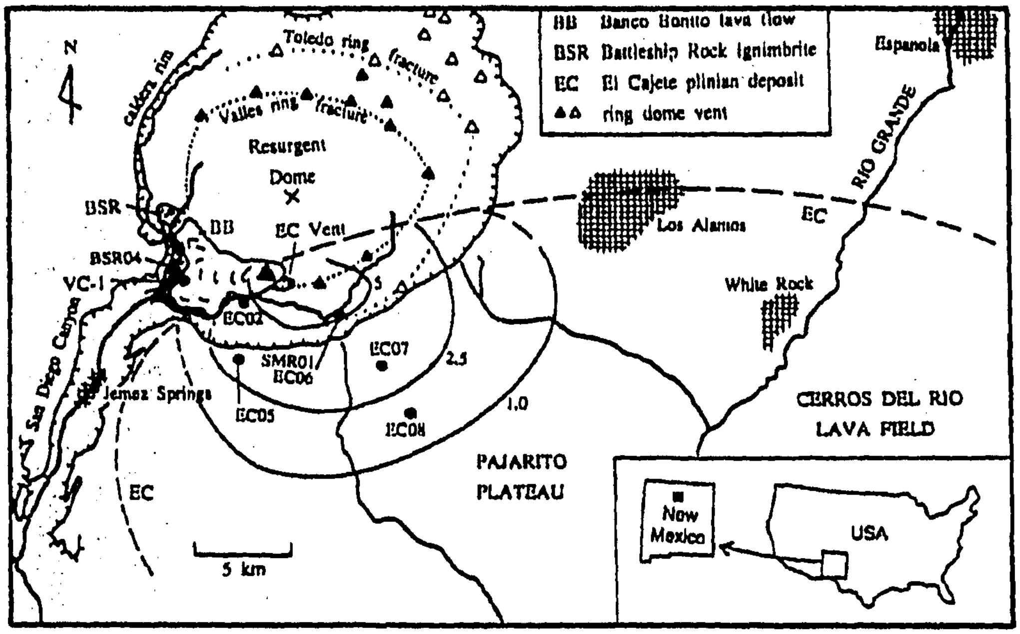


Fig. 1. Localities of the samples collected for ESR dating as shown by solid circles. Isopachs of El Cajete pumice fall deposit are shown in meters. The figure is partially modified after Self et al. (1988).

1986, 1988, 1991) since the original definitions of Bailey et al. (1969). Besides obvious uses for the magmatic, tectonic, and geomorphic evolution of the Valles caldera, the age of the El Cajete pumice eruption is very significant because it forms a widespread blanket of tephra throughout the southeastern Jemez Mountains and can construin the age of Quaternary faulting and erosion (Gardner and House, 1987; Albrecht et al., 1993).

All of the youngest rhyolites contain quartz as a primary phenocryst (Bailey et al., 1969; Gardner et al., 1986). Because ESR dating was used successfully to date quartz at other Quaternary tephra deposits (Imai et al., 1985; Shimokawa and Imai, 1987; Imai and Shimokawa, 1988), we have determined the thermal stabilities of Al and Ti centers in quartz from pumice of the El Cajete and Battleship Rock Members of the Valles caldera. Particular emphasis was given to samples of the El Cajete pumice because this unit was partially deposited outside the caldera where no hydrothermal activity of post-caldera age has occurred. Our ESR dates indicate that the El Cajete and Battleship Rock Members are of approximately the same age (53–59 ka) and younger than previously thought using fission-track and ^{39}Ar-^{40}Ar methods (Self et al., 1991).

2. Geologic background

The eruptive history of the Jemez volcanic field has been the subject of many investigations but the Valles caldera has been a focus of particular interest (Bailey et al., 1969; Smith et al., 1970; Gardner et al., 1986; Self et al., 1991). The Valles caldera is a 22-km-diameter collapse depression that formed at 1.14 Ma during eruption of the Tshirege Member of the Bandelier Tuff (Smith and Bailey, 1968; Spell et al., 1990). Soon after caldera formation, a central resurgent (structural) dome grew in the approximate center of the caldera. A sequence of no less than 14 rhyolite domes, flows, and pyroclastic deposits was erupted from about 1.05 to 0.13 (?) Ma in the caldera moat surrounding the resurgent dome (Doell et al., 1968; Gardner et al., 1986). Some of the moat rhyolites are buried by moat sedimentary rocks and younger moat eruptions (Goff et al., 1986). Hydrothermal activity is pervasive in the south-

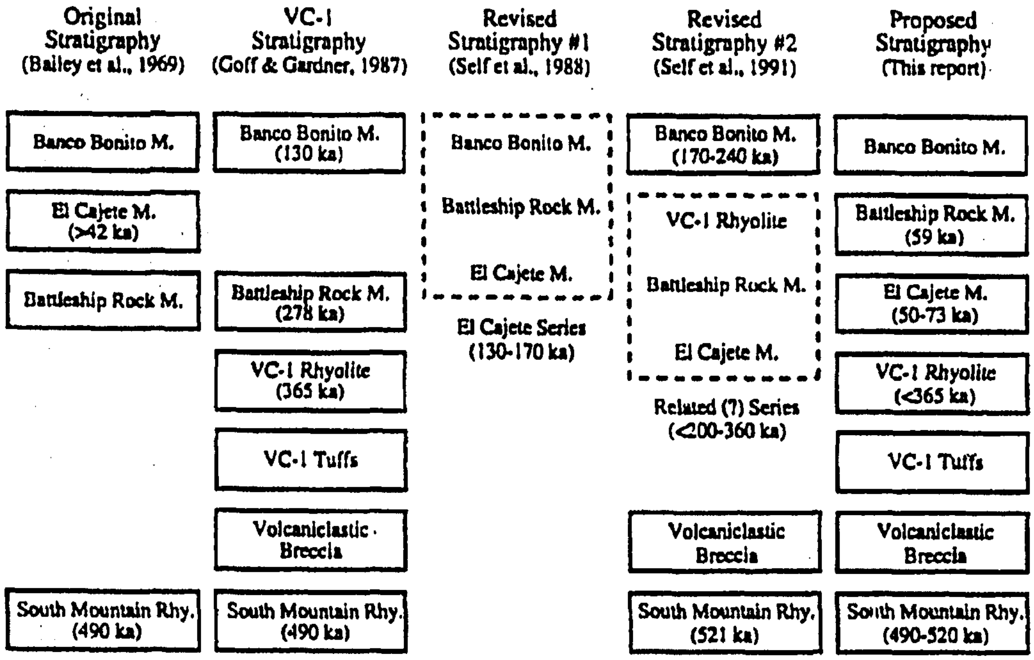


Fig. 2. Chart showing the evolution of stratigraphic interpretations for geologic units in the southern moat zone of Valles caldera, New Mexico. The VC-1 cores contain tephra units whose age and correlation with surface exposures are not resolved. The ESR dates indicate that the Battleship Rock and El Cajete Members are approximately the same age as indicated by Self et al. (1988) but are considerably younger than proposed by Self et al. (1991). The stratigraphy proposed in this report retains most of the concepts developed by Bailey et al. (1969), Goff and Gardner (1987), and Self et al. (1988).

western sector of the caldera (Goff et al., 1992) and has been continuously active for the last 1 million years (Goff and Shevenell, 1987). In their early K-Ar study of the Valles caldera, Doell et al. (1968) noted that hydrothermal alteration was a possible influence on some of their (inconsistent!) results. Although most outcrops and cores of the youngest rhyolites do not appear to be hydrothermally altered, the initial ESR study of the Valles Rhyolite by Ogoh et al. (1993) suggested that modest temperature anomalies (about 70°C) have occurred at very shallow levels in the southern caldera moat in the recent past.

The original stratigraphy of the three youngest units of the Valles Rhyolite was defined by Bailey et al. (1969) as (top to bottom) Banco Bonito Member (black, glassy, porphyritic obsidian), El Cajete Member (white to very pale orange, pyroclastic fall, flow, and surge deposits), and Battleship Rock Member (grey to tan, lithic-rich ignimbrite). The original stratigraphic definitions changed dramatically after 1986 due to numerous reinterpretations of field relations, the impact of discoveries in corehole VC-1, and the acquisition of various dates (Fig. 2).

VC-1, the first corehole drilled in Valles caldera under the U.S. Continental Scientific Drilling Program, was sited in the southwestern moat zone of the caldera and provided 856 m of continuous core of intra-caldera volcanic and sedimentary rocks (333 m) and pre-caldera Paleozoic and Precambrian rocks (523 m) (Goff et al., 1986; Goff and Gardner, 1987; Geissman, 1988; Hulen and Nielson, 1988). A key observation regarding the site of VC-1 is that it is located in a sector of the caldera moat where the ring-fracture system and the pre-caldera Jemez fault zone intersect. As a result, there has been considerable erosion and deposition of caldera-fill rocks in this sector that was previously unrecognized (Goff et al., 1986). About 300 m south of VC-1, 35 m of Banco Bonito obsidian directly overlies the nonwelded top of the Battleship Rock ignimbrite. However, in VC-1 the Banco Bonito is 149 m thick and overlies 11.9 m of tephra deposits of debated origin and stratigraphic assignment (Goff and Gardner, 1987;

Goff et al., 1989; Self et al., 1988, 1991). Much of this tephra deposit resembles nonwelded Battleship Rock ignimbrite. No fall, flow, and surge deposits similar to the El Cajete Member occur in this horizon.

One of the significant finds in VC-1 was discovery of another black, glassy, porphyritic obsidian flow (VC-1 Rhyolite) having a thickness of 20.0 m and underlying a poorly-developed soil near the base of the (debated) tephra deposits. The VC-1 Rhyolite has no known surface exposure in the caldera; thus it is impossible to relate its stratigraphic position to other young rhyolites except in VC-1. VC-1 obsidian breccia clearly overlies a well-developed soil that formed at the top of a sequence of three pyroclastic flow deposits (VC-1 Tuffs). The VC-1 Tuffs overlie another well-developed soil at the top of a volcaniclastic sequence which includes flow-breccia of South Mountain Rhyolite at the base. The contact of caldera-fill rocks with underlying Permian Abo Formation occurs at 333 m depth.

Tephra deposits in VC-1 are not distinct enough to make positive correlations with surface outcrops. The youngest rhyolites including VC-1 Rhyolite and VC-1 Tuffs have surprisingly similar petrography and major/trace element chemistry (Gardner et al., 1986). All of the youngest rhyolites include xenocrystic material that produces spurious K-Ar and ^{39}Ar-^{40}Ar dates (Spell and Harrison, 1993). As a result of these uncertainties and different interpretations, the stratigraphy has evolved as shown in Fig. 2 but no interpretation is accepted by all geologists who work in the caldera.

3. Previous age determinations of the youngest rhyolites

The youngest post-caldera rhyolites are located in the southern moat zone of Valles caldera and consist of domes, flows, and pyroclastic deposits <0.5 Ma (Doell et al., 1968; Bailey et al., 1969; Gardner et al., 1986; Geissman, 1988; Goff et al., 1989; Spell and Harrison, 1993). The ages of these youngest rhyolites have been previously investigated by ^{14}C, fission-track, K-Ar, ^{39}Ar-^{40}Ar, U-Th disequilibrium, and ESR methods (above references; Marvin and Dobson, 1979; Miyaji et al., 1985; Self et al., 1988, 1991; Ogoh et al., 1993) but none of these methods yield consistent nor geologically reasonable results.

Doell et al. (1968) reported a K-Ar age of 490 ± 15 ka for South Mountain Rhyolite but did not report any ages for the overlying youngest rhyolites, presumably because they were too young for K-Ar dating. Goff and Gardner (1987) obtained a K-Ar age of 600 ± 100 ka on South Mountain Rhyolite breccia from the bottom of the moat volcanic section of VC-1 (Fig. 2). A more recent K-Ar date of 507 ± 15 ka has been determined by Spell and Kyle (1989) and successive ^{39}Ar-^{40}Ar ages of 517 ± 14 and 521 ± 4 ka have been listed by Spell et al. (1990) and Spell and Harrison (1993), respectively. The consistent ages reported for this distinctive unit are important because the youngest rhyolites overlie South Mountain Rhyolite in several key outcrops in the caldera moat (Smith et al., 1970; Self et al., 1988; Goff et al., 1989).

The VC-1 Rhyolite has a K-Ar date of 365 ± 61 ka (Gardner et al., 1986) and ^{39}Ar-^{40}Ar dates of 518 to 631 ka ($n = 5$, Spell and Harrison, 1993). The range of ^{39}Ar-^{40}Ar ages suggests that xenocrystic material is present in this unit. The Battleship Rock Member has a K-Ar date of 278 ± 2 ka (Goff et al., 1989), but fission-track ages of 180 ± 70 to 130 ± 70 are also reported for this unit (Miyaji et al., 1985).

Bailey et al. (1969) found a carbonized log in a fresh roadcut through pumice of the El Cajete Member along state highway 4 but the ^{14}C age was >42 ka. More recently, S. Reneau and J.N. Gardner (unpubl. data, 1992) have dated additional logs found in a pumice mine 200 m north of highway 4 and obtained ages of >50 ka. Miyaji et al. (1985) obtained a fission-track age of 170 ± 70 ka. Self et al. (1988) incorrectly reported a U-Th disequilibrium date of about 150 ± 40 ka. Self et al. (1991) and Spell and Harrision (1993) report ^{39}Ar-^{40}Ar ages of 519 to 923 ka ($n = 4$) indicating that xenocrystic material is also present in this unit.

Marvin and Dobson (1979) obtained a fission-track age of 130 ± 100 ka for obsidian of the Banco Bonito Member, undisputably the youngest of all post-Valles caldera eruptions. Miyaji et al. (1985) reported another fission-track age of 140 ± 50 ka. Self et al. (1991) and Spell and Harrison (1993) list nine ^{39}Ar-^{40}Ar dates ranging from 205 to 1300 ka. This latter age range is perhaps the best evidence for xenocrystic material being present in this unit (as well as other youngest rhyolites) and the problem is discussed by Spell and Harrison (1993).

In a previous ESR dating study (Ogoh et al., 1993), quartz separates obtained from outcrops of the Banco Bonito, El Cajete, and Battleship Rock Members within the southern moat of the caldera yielded ages ≤45 ka. Quartz separates were also obtained from pumice of the VC-1 core in units identified as the Battleship Rock Member, the Upper VC-1 Tuff, and Middle VC-1 Tuff (Goff and Gardner, 1987; Geissman, 1988). However, it was found that successively deeper units in VC-1 yielded successively younger ages (as young as 19 ka); thus it was suspected that thermal annealing from past and/or present hydrothermal activity was causing the ESR ages to be too young. For these reasons, we collected additional samples of El Cajete pumice form locations outside the caldera to eliminate effects of hydrothermal alteration and thermal annealing and to perform heating experiments of Al and Ti impurity centers.

4. Electron spin resonance dating

ESR (electron spin resonance) detects unpaired electrons in samples. Unpaired electrons are created in minerals by natural radiation and are trapped at some defect and impurity sites in the crystal structure (Ikeya, 1993): for example, an Al atom replacing Si traps an electronic hole to form an Al center (Griffith et al., 1954), and a Ti atom replacing Si traps an electron to form a Ti center (Wright et al., 1963) in quartz. An ESR signal intensity corresponds to the amount of unpaired electrons which have been accumulated in the mineral since it was crystallized. The natural radiation dose rate produced by U, Th, and their daughter elements, and K is calculated by using the concentrations of these elements or measured by thermoluminescence dosimeters. The age is obtained by dividing the total accumulated dose (or equivalent dose, D_E) determined by ESR measurements by the annual dose (D) from natural radiation.

The ESR method has been previously applied to determine the age of many minerals and deposits, such as stalactites of calcite (e.g., Ikeya, 1975), corals of aragonite (e.g., Ikeda et al., 1991), tooth enamel of hydroxyapatite (e.g. Grün and Invernati, 1985), and shells of calcite and of aragonite (Ikeya and Ohmura, 1981), as well as quartz and plagioclase in volcanic rocks and ashes (Imai et al., 1985; Shimokawa and Imai, 1987). The thermal stability of the defects limits the age range to be dated up to about 2 Ma (e.g., Shimokawa and Imai, 1987). The younger age limit depends on the sensitivity of the ESR spectrometer, being around several thousand years for recent commercial ones (Ikeya, 1988).

The signals of Al centers in quartz were used to obtain ESR ages of volcanic tephras in the first study (Imai et al., 1985). The signals of Ti centers in quartz were also used in subsequent studies (Imai and Shimokawa, 1988). Some fundamental results on thermal stabilities of paramagnetic defects and impurity centers were reported by Toyoda and Ikeya (1991). However, characteristics of all the centers, such as thermal stabilities, response for irradiation, and reaction between the centers, have not been well established yet.

5. Sample sites and sample preparation

We collected 2 kg of pumice from the type locality of the Battleship Rock Member (BSR04) and 2 kg of rock from the easternmost roadcut of South Mountain Rhyolite exposed along highway 4 (SMR01) as shown in Fig. 1. We also collected 2 kg of pumice from five localities (EC02, EC05, EC06, EC07, and EC08) of El Cajete Member. These locations were chosen to be both inside and outside the caldera to eliminate any bias due to post-caldera hydrothermal alteration (Smith et al., 1970; Goff et al., 1989). Original pumice and rhyolite were crushed in a mortar and were sieved. Porous grains larger than 1 mm size were removed by using a heavy liquid (sodium polytungstate solution). A portable magnetic separator removed the grains containing magnetic minerals. Quartz grains of 1 to 2 mm were handpicked. Finally, the extracted grains were etched in 20% hydrofluoric acid for 2.5 hours to remove defects near the surface caused by alpha emitters in the original rock matrix. Six to eight aliquots of 90 to 120 mg from each sample were prepared after the grains were crushed to 75 to 250 μm.

6. Experimental procedure for ESR dating

ESR signals from Al and Ti centers were observed with a commercial X-band ESR spectrometer (JEOL RE-1X) at liquid nitrogen temperature (77K) with a

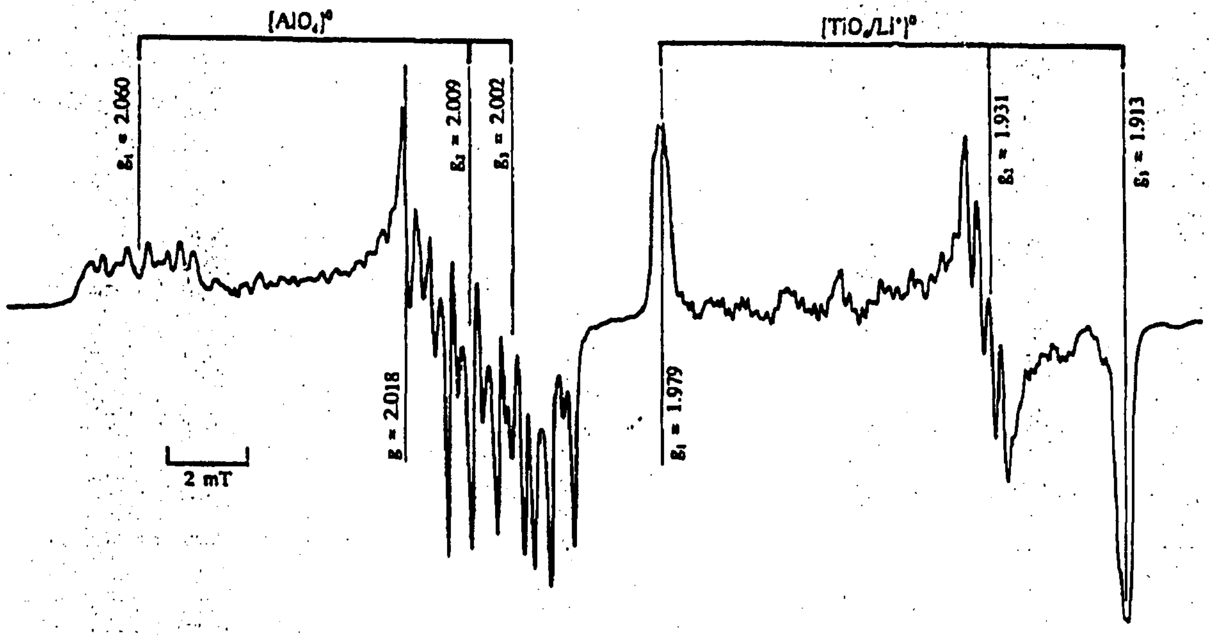


Fig. 3. ESR signals observed at liquid nitrogen temperature (77K) in quartz extracted from SMR01. ESR signals due to two impurity centers are observed; Al center, $[AlO_4]^0$, where an Al atom replacing Si atom traps an electronic hole, and Ti center with Li^+, $[TiO_4/Li^+]^0$, where a Ti atom replacing Si atom traps an electron.

100-kHz field modulation of the amplitude at 0.1 mT and with a microwave power of 5 mW (Fig. 3). These signals were caused by Al centers, $[AlO_4]^0$ (McMorris, 1971), and by lithium compensated Ti centers, $[TiO_4/Li^+]^0$ (Toyoda, 1992).

A ^{60}Co source was used to irradiate samples at a dose rate of 34 Gy/h. Signal growth was fitted to a straight line or to a saturation curve obtained by the least squares method using a fortran program package named SALS (Nakagawa and Oyanagi, 1982). Total accumulated doses (D_E) were determined by extrapolating the growth line/curve to the zero ordinate. The error in D_E was estimated by considering the errors of the parameters of the line/curve and the correlation between them.

Annual dose (D) was calculated for each sample using the concentrations of K_2O, U, and Th (Table 1) that were determined by instrumental neutron activation analysis of the whole rock rhyolite from which the quartz was separated (J.N. Gardner, unpubl. data). The decrement of β ray dose was considered for the diameter of quartz grains of 1.5 mm to be 46% for ^{232}Th chain, 50% for ^{238}U chain, and 52% for ^{40}K using fig. A-2 in Grün (1989) (original data by Mejdahl, 1979). The error in the annual dose is estimated to be 6% by considering the errors in the concentrations of K, U, and Th. Cosmic dose rate was estimated to be 0.30 mGy/y for four samples of El Cajete pumice (EC05, EC06, EC07, and EC08), which have been in outcrop, and to be 0.21 mGy/y for other samples which have

Table 1
Concentrations of radioactive elements obtained by neutron activation analysis (J.N. Gardner, unpublished data), water content, and calculated dose rates for the present samples

Sample	U (ppm)	Th (ppm)	K_2O (%)	Water content	Cosmi dose rate (mGy/y)	D (mGy/y)
South Mountain Rhyolite	8.2	29.9	4.67	1.8	0.21	5.06
El Cajete Pumice (EC02)	5.4	19.7	4.22	3.6	0.21	3.87
El Cajete Pumice (Others)	5.4	19.7	4.22	3.6	0.30	3.96
Battleship Rock	5.4	19.1	4.00	3.5	0.21	3.72

been buried (SMR01, EC02, BSR04) using fig. A-4 in Grün (1989) (original data by Aitken, 1985 and by Prescott and Stephan, 1982) where the elevation is 2000 m. ^{222}Rn and ^{220}Rn loss were assumed to be 50%. Radioactive disequilibrium between ^{238}U and ^{230}Th was neglected.

Table 2
The results of ESR dating using the signals of Al and Ti centers and stable component of Ti centers for Valles Rhyolite

Sample	before heating								after heating			
	Al center				Ti center				Ti center			
	D_{II} (Gy)		Age (ka)		D_{II} (Gy)		Age (ka)		D_{II} (Gy)		Age (ka)	
SMR01	1700	+300 / −200	330	+60 / −50	2200	+200 / −170	440	+50 / −40	1)		1)	
EC02	203	+58 / −47	52	+15 / −13	338	+17 / −16	87	±7	285	+43 / −27	73	+11 / −7
EC05	233	+37 / −32	59	+10 / −9	309	+34 / −32	78	+10 / −9	191	+23 / −16	49	+6 / −4
EC06	163	+18 / −16	41	±5	290	+18 / −17	73	±6	213	+34 / −24	53	+9 / −6
EC07	230	+41 / −36	58	+11 / −10	258	+20 / −19	65	±6	178	+23 / −17	45	+6 / −4
EC08	181	+24 / −22	46	+7 / −6	297	+8 / −7	75	±5	228	+26 / −18	57	+6 / −5
BSRP	127	+11 / −10	34	+4 / −3	170	±6	46	±3	220	+24 / −19	59	+6 / −5

1) D_{II} and age were not obtained because the stable component was not enhanced by γ ray irradiation. Its minimum age would be 440 ka, which is obtained from Ti centers with no heat treatment.

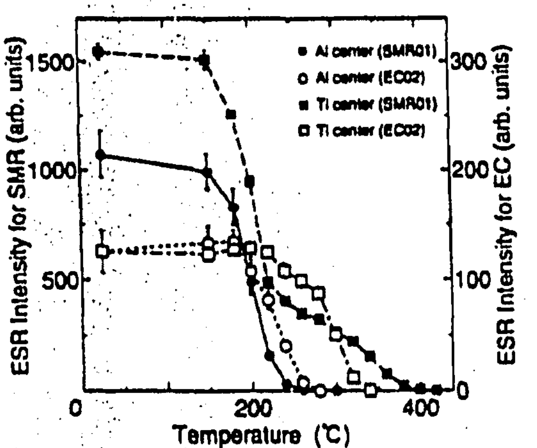


Fig. 4. The change in signal intensities of Al and Ti centers on stepwise heating of SMR01 and of EC02. Both intensities decreased around 200°C. However, the intensity of Ti centers shows a second step above 250°C indicating that Ti centers have two components; thermally stable one and less stable (temperature sensitive) one.

7. Results and discussion

7.1. ESR ages with no heat treatment

Signal enhancements of Al and Ti centers by artificial γ ray irradiation are shown in Fig. 5a–c where total accumulated doses (D_E) were determined. Table 2 summarizes the results of ESR dating. The ages obtained by Al centers are systematically younger than the ones by Ti centers. Such systematic differences between ESR ages were also observed by Shimokawa and Imai (1985). No effect of hydrothermal activity was observed because there is no systematic change in the ESR ages due to the sampling localities of El Cajete pumice (see Fig. 1).

7.2. Thermal stabilities of Al and Ti centers

Two aliquots of quartz grains from SMR01 and EC02 were isochronally heated between 100 and 400°C with a duration of 15 minutes to examine thermal stability of the paramagnetic centers (Fig. 4). The signal intensities of Al and Ti centers were measured after each temperature step.

Both signal intensities of Al and Ti centers in SMR01 decreased on heating around 200°C (Fig. 4). The figure also shows that the decrements of the signal intensities of Ti centers are less around 250°C than those below 200°C making a clear second step. This behavior indicates that Ti centers have two components; a less stable (temperature sensitive) one and a stable one. The same tendency was observed for Ti centers in EC02 where the amount of decrement in the first step is small.

The coefficients of the signal decrease in the temperature steps were calculated and plotted on an Arrhenius diagram for Al centers and for Ti centers of both less stable and stable components assuming second order decay kinetics (Toyoda and Ikeya, 1991). The potential signal decrement in the geologic time scale was estimated by extrapolating the correlation to the ambient temperature of the samples. Considering the error in the extrapolation, it is possible that the signal intensities of Al center and of less stable component of Ti center may have been decreased considerably, while no decrease must have occurred for stable component of Ti centers.

If part of both Al and less stable Ti centers have decreased while the samples had been buried, the ESR age obtained for Al center would be less than the one for Ti centers because Ti centers have a stable component which has never been affected. The systematic age difference observed between Al center and Ti centers might indicate such decrement of the centers.

The decay on heating of less stable component of Ti center appears to be correlated with the decay of Al center as shown in Fig. 4. It may indicate that electronic holes trapped at Al centers are released on heating to recombine with electrons trapped at Ti centers. The stable component of Ti center decays at higher temperature when electronic holes are unstabilized and released from some other centers. In other words, natural and artificial radiation may create two types of electron-hole pairs. One is Ti center (electron) and Al center (hole) and the other is Ti center (electron) and unknown hole center. The former pair is thermally less stable than the latter.

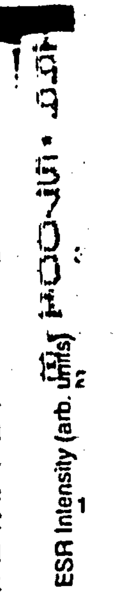
Using this logic, thermal stabilities of paramagnetic centers depend not only on their own characteristics but also on that of other centers with which electrons/holes at the centers recombine. It implies that thermal stabilities of paramagnetic centers in quartz are different for individual samples. For example, a part of Ti center is more stable than Al centers in the present sample, while the opposite stabilities were observed in a case of granite (Toyoda and Ikeya, 1991).

7.3. ESR dating with stable component of ti centers

The above experimental results and discussions indicate that only the stable component of Ti centers would be useful for ESR dating of the quartz in Valles Rhyolite. The experimental procedures for ESR dating were repeated for all samples after they were heated at 260°C to extract the stable component. The signals of the Al center disappeared on heating for all samples. The ESR intensities of Ti centers are plotted as a function of artificial γ ray dose (Fig. 5a-c). Obtained D_E's and ages are shown in Table 2.

The intensity of Ti centers in SMR01 shows no enhancement after heating (Fig. 5a) resulting in no D_E and age obtained. This would be because the intensity of stable Ti centers is saturated in this dose range. Indeed, after SMR01 was heated at 420°C for 15 minutes to anneal all ESR signals, the stable component was regenerated by γ ray irradiation bellow 1 kGy but was saturated above 1 kGy. Part of Al and Ti centers in this sample may have decreased while the sample had been buried, as implied by the difference between ages for Al and Ti centers before heating. Although the amount of decay in the past cannot be estimated, the minimum estimated age would be 440 ka for SMR01 by D_E obtained for Ti center before heating. If there had been no decay for Ti centers in the past, the observed intensity should have been larger, therefore, we should have obtained larger value of D_E.

The intensity of the stable component of Ti centers was enhanced by γ ray irradiation (Fig. 5b, c) for BSR04 and EC samples, resulting in D_E's and ages as shown in Table 2. The stable component would have never been affected by ambient temperature even in the hottest days in summer. The age of BSR04 using the stable component is older than the one obtained by using total amount of Ti centers. It is because the less stable component, part of which may have decreased while the sample had been buried, was removed by heating the samples. On the other hand, the ages of EC samples obtained after heating are younger than the ones before heating. The following experiment was made to check the thermal behavior of Ti centers. After an aliquot of EC02 was heated at 420°C for 15 minutes to anneal all ESR signals, the sample was irradiated by



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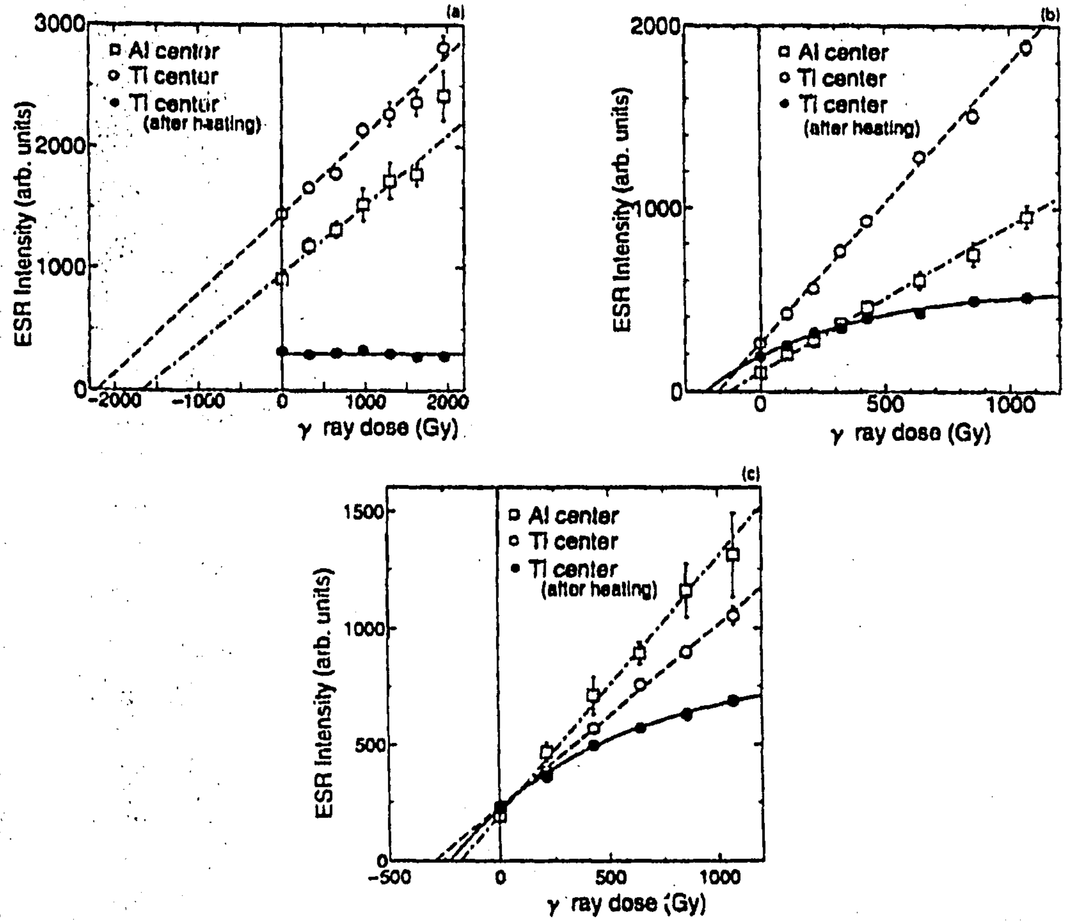

Fig. 5. The enhancement by artificial γ ray irradiation of ESR intensities of Al centers and of Ti centers both before and after heating at 260°C (a) in SMR01, (b) in BSR04, and (c) in EC08. The regression line and saturation curves are obtained by the least square fitting. Total accumulated doses (D_E) are obtained by extrapolating the line/ curve to the zero ordinate.

ray at 200 Gy. The signal intensities of Ti centers were measured both before and after re-heating at 260°C for 15 minutes. The intensity after heating was slightly larger than before heating. This experimental result indicates that an unknown electronic process transfers electrons from some unstable states on heating to Ti replacing Si to form Ti centers. If it is true, such a process may have occurred in the quartz in El Cajete pumice while it had been buried, resulting in overestimation of D_E by the conventional method. Heat treatment after γ ray irradiation prior to ESR measurement, as proposed in this paper, can simulate this electronic process as well as remove the less stable component.

8. Geologic implications

The work of Ogoh et al. (1993) has shown that some ESR signals are thermally unstable; thus great care must be take to insure that samples used for ESR studies have not been subjected to thermal or hydrothermal stress. Temperatures as low as 60°C for 10 ka could effect ESR dates on quartz as much as 30%, as implied by the present study.

By evaluation of the thermal effects on quartz separates, we have determined ESR ages of 45 to 73 ka for the El Cajete Member and 59 ± 6 ka for the Battleship Rock Member of the Valles Rhyolite. Considering

Reneau and Gardner's ^{14}C age of >50 ka (unpubl. data), the eruption age of El Cajete Member would be 50 to 73 ka (Fig. 2). The weighted average of the five El Cajete samples yields an age of 53±6 ka where ISOPLOT program of K.R. Ludwig is used (D.A. Sawyer, 1994, personal communication). These ages are considerably younger than most of the other age determinations made on this unit. By comparison, the ESR age of the South Mountain Rhyolite is >440 ka (Ti center before heating) which is reasonably close to the presently accepted age of 520 ka (Spell and Harrison, 1993).

Because of the Banco Bonito Member undiputably overlies the El Cajete Member, the Banco Bonito obsidian flow is <73 ka. It is worth noting that this obsidian flow has a very youthful appearing upper surface with well-defined pressure ridges up to 20 m deep. The ESR ages are consistent with the present state of preservation (Fink and Manley, 1987). If the ages are correct, it is very apparent that the recent ^{39}Ar-^{40}Ar ages of both the El Cajete and Banco Bonito Members presented by Self et al. (1991) are too old and that their recent revisions to the post-0.5 Ma units of the caldera are again in error. These older ages are so variable that they must be caused by abundant xenocrysts in the units derived from older rocks beneath the caldera (Spell and Harrison, 1993).

Additional efforts are still needed to clarify the ESR ages by determination of the radon loss rate as well as by revealing the characteristics of Al and Ti centers in quartz during heating and irradiation. Radon loss of 0% or 100% yields about 30% younger or older ages, respectively.

9. Conclusions

Quartz phenocrysts in Quaternary tephras and possibly other types of volcanic deposits can be used to obtain ESR dates. Sampling sites must be evaluated to eliminate effects of thermal and hydrothermal stress. Ti centers in quartz have a thermally less stable component and a stable component for at least three members of the Valles Rhyolite. The ESR signal of the stable component of Ti centers yields an age of 53±6 ka for the El Cajete Member (Its ^{14}C age indicates <50 ka.) and an age of 59±6 ka for the Battleship Rock Member. If these dates are correct, then the El Cajete and Battleship Rock Members are closely associated in time with the overlying Banco Bonito Member as originally proposed by Bailey et al. (1969) and Self et al. (1988). In addition, the Battleship Rock ignimbrite is younger and distinct from the VC-1 Tuffs as proposed by Goff and Gardner (1987) and the El Cajete and Banco Bonito Members are both younger than indicated by the most recent revisions of Self et al. (1991), although some observations in the tephra deposits remain to be clarified.

The age of most recent volcanism in the Jemez Mountains is probably much younger than previously thought. If so, our results have implications for the evolution of post-Valles caldera magmas, for the geomorphic evolution of the caldera moat zone, and for the age of faulting in this tectonically active region.

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