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QUARTZ IN POST-CALDERA RHYOLITES OF VALLES CALDERA, NEW MEXICO: ESR FINGER PRINTING AND DISCUSSION OF ESR AGES

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Abstract—The eruption ages and stratigraphic sequence of the youngest members of the Valles Rhyolite are of interest for understanding the Quaternary volcanic history of the Valles caldera and for investigating volcanic hazards. ESR signals due to three types of Ti centers in quartz were employed to clarify the debated stratigraphic sequence found in the VC-1 core. Samples of xenocrystic quartz from the Banco Bonito, El Cajete and Battleship Rock Members have distinctive signal patterns, indicating that each magma had captured quartz grains from different sources, although the major and trace chemical composition of the magmas are similar. Comparing the patterns observed in the samples from the VC-1 core with those in the samples from outcrops, our results generally support the stratigraphic assignments of volcanic units made by Goff and Gardner (1987). The possible problems of ESR ages recently published by Toyoda et al. (1995) are also discussed, concluding that ESR ages of 53±6 ka for the El Cajete Member and 59±6 ka for the Battleship Rock Member, supported by the recent TL age on the El Cajete Member, are presently the best estimates of the eruption ages of these units.

INTRODUCTION

The Jemez Mountains volcanic field, New Mexico, has a record of continuous volcanism for more than 13 Ma (Gardner et al., 1986). Numerous investigations have aimed to resolve the detailed history of volcanism and to evaluate the hydrothermal systems of the Valles caldera (Doell et al., 1968; Gardner et al., 1986; Spell et al., 1990; WoldeGabriel and Goff, 1989). One present topic of interest is to determine the date of most recent volcanism in the caldera. K-Ar, ^{40}Ar-^{39}Ar, fission-track, ESR (electron spin resonance), and TL (thermoluminescence) dating methods have been employed to obtain the ages of eruptions that produced the youngest tephras (e.g., Spell and Harrison, 1993; Miyaji et al., 1985; Toyoda et al., 1995; Reneau et al., 1996). While the ^{40}Ar-^{39}Ar dating method indicates contamination of radiogenic ^{40}Ar from xenocrystic material (Spell and Harrison, 1993), ESR and TL methods reveal that the ages of the youngest volcanism are much younger than previously thought (Toyoda et al., 1995; Reneau et al., 1996). Wolff and Gardner (1995) claimed the necessity to monitor Valles caldera for volcanic hazards, with discussion based on the new ages, recent seismic activity (Cash and Wolff, 1984), and seismic velocity anomalies (Lutter et al., 1995). In this paper, previous work on radiometric ages, including ESR dates, is reviewed together with discussion of possible problems. New evidence is presented using ESR signal patterns ("fingerprints") in quartz xenocrysts to show that VC-1 Rhyolite is closely related to Battleship Rock ignimbrite, whereas VC-1 Tuff is probably distinct from Battleship Rock ignimbrite.

ESR DATING METHOD

Ionizing radiation creates radicals and/or pairs of electrons and electronic holes in solids. Some of the electrons and holes are trapped at, or stabilized near impurities or lattice defects as quasi-stable states. If the states are paramagnetic (with unpaired electrons), they are detectable by the ESR (electron spin resonance) method. Those quasi-stable states are unstabilized when heated, and emit light when they recombine (thermoluminescence, TL, Aitken, 1985). Irradiation with light of a specific wavelength also causes the electrons and holes to recombine and emit light (optical stimulated luminescence, OSL, Huntley et al., 1985). In these three methods, the signal intensities correspond to the amount of unpaired electrons or recombining electron-hole pairs, and thus, to the amount of radiation delivered to the solid during its burial history. When a mineral is irradiated in nature, these methods quantify the accumulated natural radiation dose (D_E). Practically, the sample is irradiated with γ or β rays to create additional signals artificially in order to know the rate of signal increase in the mineral per unit of irradiation dose (the additive dose method). In order to deduce ages, the dose (D_E) is then divided by the dose rate (D) in the environment measured by dosimeters or calculated from U, Th, and K contents of the stratigraphic horizon where the mineral has resided.

The ESR method has the advantage that the signals can be observed without destroying the states of unpaired electrons, whereas TL and OSL methods cause the electron-hole pairs to recombine. Also, in ESR measurements, the origin of the signal is clear in many cases when referenced to previous measurements in the field of solid state physics. However, a disadvantage is that ESR can detect only unpaired electrons and that the sensitivity is currently less than TL.

The ESR dating method has successfully been applied to many minerals (Grün, 1989; Ikeya, 1993), such as calcite in speleothems (Ikeya, 1975), aragonite in fossil corals (Ikeya and Ohmura, 1983), both calcium carbonates in shells (Ikeya and Ohmura, 1981), hydroxyapatite in tooth enamel (Grün et al., 1987), gypsum from lake deposits (Ikeya, 1985), and quartz from tephra and fault gouge (Ikeya et al., 1982; Lee and Schwarcz, 1994). Quartz phenocrysts from tephras are promising material for obtaining the eruption ages because the zeroing mechanism of the ESR signals is clear. The high temperature at eruption (>600°C) erases all previous ESR signals in quartz, as is clearly shown by laboratory heating experiments (Toyoda and Ikeya, 1991).

The ESR dating of tephra was first reported by Imai et al. (1985) using Al centers in quartz, plagioclase, and volcanic glass; an Al center is an Al impurity replacing a Si site, trapping an electronic hole (Griffith et al., 1954). The obtained age for quartz was consistent with the fission track age. Yokoyama et al. (1985) used quartz out of sediments baked by lava and obtained an age of the lava flow where D_Es for Al and Ti centers coincided. The Ti center they used is a Ti ion trapping an electron and accompanying a Li ion in order to compensate the charge (Rinneberg and Weil, 1972; Toyoda, 1992, fig. 2-1d). Some natural quartz exhibits ESR signals due to Ge centers, a Ge ion replacing a Si site and trapping an electron (Anderson and Weil, 1959), and to OHC (oxygen hole centers), non-bonding oxygen associated hole with a center, analogous to the similar center in amorphous silica (Stapelbroek et al., 1979). Combining ESR ages obtained for these signals, Shimokawa and Imai (1987) showed the possibility for obtaining both eruption and alteration ages. The coinciding ESR ages for the Ge center and OHC, roughly close to the fission track age, was older than the age for the Al center, which was consistent with a TL age. They stated that the former indicates the eruption age and that the latter the alteration age. In their subsequent studies using Al and Ti centers in quartz from tephra and baked rocks, ages obtained were consistent with geologic estimates and with K-Ar ages (Imai and Shimokawa, 1988; Shimokawa et al., 1988) except for a few dates (Shimokawa et al., 1988; Imai and Shimokawa, 1989). A perfect example was obtained for a volcanic rock from New Zealand by Buhay et al. (1992), where ESR ages from Al and Ti centers coincided and the value was consistent with the ^{14}C age.

STRATIGRAPHIC SEQUENCE AND PREVIOUS RESULTS OF AGE DETERMINATIONS OF THE VALLES RHYOLITE

The stratigraphy of the youngest units of the Valles Rhyolite was first described by Bailey et al. (1969). The sequence is, from top to bottom, Banco Bonito Member (black, glassy, porphyritic obsidian), El Cajete Member (white to very pale orange, pyroclastic fall, flow, and surge deposits), Battleship Rock Member (grey to tan, lithic-rich ignimbrite), and South Mountain Rhyolite.

Since the first corehole, VC-1, was drilled in Valles caldera under the U. S. Continental Scientific Drilling Program (e.g., Goff et al., 1986), the stratigraphic assignment of the members newly found in the core and the ages have been in debate. In VC-1 at 149 m depth, the Banco Bonito obsidian flow overlies a non-welded to welded crystal-lithic tephra deposit 11.9 m thick which was assigned to Battleship Rock Member by Goff and Gardner (1987) but to part of the Banco Bonito flow by Self et al. (1991). Another black, glassy porphyritic obsidian flow with thickness of 20.0 m, named VC-1 Rhyolite, was found overlain by the above deposit. Below this obsidian flow, a tuff layer with a thickness of 117 m was also found. Goff and Gardner (1987) assigned this tuff to a new member named VC-1 Tuff but Self et al. (1991) assigned it to the Battleship Rock Member. The lowermost bed of tuff (293–298 m) in this sequence (lower VC-1 Tuff of Goff and Gardner, 1987) was assigned to the El Cajete Member by Self et al. (1991). These tuffs overlie another volcaniclastic sequence that includes flow-breccia of the South Mountain Rhyolite.

Doell et al. (1968) reported a K-Ar age of 490±15 ka for the South Mountain Rhyolite (SMR). Goff and Gardner (1987) obtained a K-Ar age of 600±100 ka on SMR breccia from the bottom of the moat volcanic section of VC-1. A more recent K-Ar date of 507±15 ka was reported by Spell and Kyle (1989) and successive ^{40}Ar-^{39}Ar ages of 517±14 and 521±4 ka were listed by Spell et al. (1990) and Spell and Harrison (1993), respectively.

The VC-1 Rhyolite has a K-Ar date of 365±61 ka (Gardner et al., 1986) and ^{40}Ar-^{39}Ar dates of 518 to 631 ka (Spell and Harrison, 1993). The K-Ar dating method assumes that Ar isotopes in the mineral had been equilibrated with air at the time of eruption. The ^{40}Ar-^{39}Ar method is more robust for partial loss or gain of Ar isotopes after the main eruptive event. However, the argon isotopes released in the temperature range where the plateau age is obtained must be equilibrated with air. The consistency of the ages for SMR occurs because the rhyolite is so porous that the exchange of Ar isotopes was easy enough to be equilibrated with air. In contrast, the VC-1 Rhyolite was very viscous for gas exchange, causing the scattering in resulting ages.

The Battleship Rock Member (BSR) has a K -Ar date of 278±2 ka (Goff et al., 1989), but fission track ages were also reported for this unit to be 130±70 ka for a pumice fall and 60 ka and 180±70 ka for an ash flow using zircon crystals (Miyaji et al., 1985). The difference in the K-Ar and the fission track ages indicate the possibility of xenocrystic contribution to Ar isotopes, whereas the scattering within the fission track ages may indicate that the tracks in the xenocrystic zircon grains had not been completely annealed at eruption.

Bailey et al. (1969) found a carbonized log in the El Cajete Member (EC) with a ^{14}C age of >42 ka. More recently, Reneau et al. (1996) obtained an age of >50 ka also by the ^{14}C method. Miyaji et al. (1985) obtained a fission track age of 170±70 ka. Self et al. (1991) and Spell and Harrison (1993) reported ^{40}Ar-^{39}Ar ages of 519 to 923 ka; the scattering indicates 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 rhyolite eruption. Miyaji et al. (1985) reported another fission-track age of 140±50 ka. Self et al. (1991) and Spell and Harrison (1993) listed nine ^{40}Ar-^{39}Ar dates of 200 ka to 1.100 Ma, perhaps the best evidence for xenocrystic material being present in this unit.

The scattering of fission-track ages of BSR (Miyaji et al., 1985) may result because the annealing of zircon of xenocrystic origin was not complete for some grains, as discussed above. In contrast, ESR signals of quartz have thermal stabilities much less than fission tracks in zircon (Toyoda and Ikeya, 1991), making it possible to obtain the eruption ages even if the grains are xenocrystic in origin.

ESR AGES

The first ESR study on these youngest members of the Valles Rhyolite was done by Ogoh et al. (1993), producing ages for outcrop samples ranging from 32 to 45 ka, considerably younger than previous ages. The ages obtained from the Al center are systematically younger than those from the Ti (Ti-Li) center. The authors argued that some thermal disturbance on ESR signals was indicated by these systematics because they are consistent with the fact that the thermal stability of the Al center for this quartz is less than that of the Ti center. The ESR ages of SMR were also much younger than the previous consistent K-Ar and ^{40}Ar-^{39}Ar ages. The thermal effect was clearer for the samples from the VC-1 core because the ages were younger for the samples from deeper levels where the present ambient temperatures are higher at greater depths, up to 60°C. It was revealed that such low temperatures may affect the ESR signals if the temperature lasts for a long time (e.g., 10^4 years, Toyoda and Ikeya, 1994). Ogoh et al. (1993) raised three possibilities for their results: (1) the ESR ages are almost correct even though they may be affected by small thermal effects; (2) the ESR signals are not stable at the present ambient temperature; (3) a recent thermal event (10-40 ka) had partially erased the ESR signals.

In order to clarify these possibilities, Toyoda et al. (1995) analyzed several EC samples from inside and outside of the Valles caldera because the near-surface intracaldera environment records thermal disturbances due to hydrothermal activity (≤1 Ma) whereas no such events occurred on the southeastern flank of the caldera (Fig. 1). No systematic difference in ages between these two groups of samples were observed. However, ESR ages from the Al center are still systematically younger than those from the Ti center. Precise annealing experiments made on two of the samples (one from EC, the other from SMR) showed that the Ti center has two components, a stable and less stable (temperature sensitive) one, whereas only one component exists for the Al center (Toyoda and Ikeya, 1994). We considered high ambient temperature in summer (up to 60°C) as the cause of this systematic difference in ages. Using the activation energy and pre-exponential factors experimentally obtained, the maximum thermal decay for the centers were estimated (Toyoda and Ikeya, 1994) to be up to 50-80% for the Al center and up to 40-60% for the less stable component of the Ti center, whereas no effect could be detected for the stable component of the Ti center. Therefore, we used the stable component of the Ti center, extracted by heating at 260°C for 15 min, for dating these samples. The resulting ages are 53±6 ka for EC and 59±6 for BSR (with 1σ error). We believe these ages are the most reasonable at present for the eruption ages of the youngest members of the Valles Rhyolite. The stable component of the Ti center did not increase by artificial γ ray irradiation for SMR, probably due to the saturation effect. The age from the Ti center without heating is 440 ka and should be considered the minimum ESR age, being relatively consistent with the presently accepted age of 520 ka (Spell and Harrison, 1993).

Our ESR ages have been recently supported by TL analyses reported by Reneau et al. (1996). They analyzed soils overlain by EC pumice and obtained ages of 48±5 to 61±5 ka, within our error range of the EC age. Our ESR age of BSR is also consistent with 60 ka, one of the two fission track ages obtained by Miyaji et al. (1985), which has been ignored by most authors.

Although many efforts have been devoted to obtaining reliable ESR ages, we feel that the following experiments could improve the ESR ages: (1) analyze samples free from the thermal disturbances caused by high ambient temperature in summer and by possible hydrothermal activity; and (2) determine the "in-vivo" value of the environmental dose rate; it is possible that the dose rate varies from site to site, contributing to the variation in ages of EC reported by Toyoda et al., (1995). The latter measurement also determines the radon loss rate, which Toyoda et al. (1995) assumed to be 50%. Another effort is needed to obtain the eruption age of the Banco Bonito Member, previously reported to be 45±2 ka by Ogoh et al. (1993). This unit should exhibit the youngest age of the Valles Rhyolite because of its stratigraphic position. For the ESR method to be more widely used, many more examples are needed where ESR dates of tephra coincide with those obtained by other dating methods such as ^{14}C and fission track methods.

USE OF ESR SIGNALS AS FINGER PRINTS OF QUARTZ IN TEPHRA AND LAVA

Stratigraphic sequence

Because of the similarity of the whole-rock chemical composition of each member (Self et al., 1988; Spell and Kyle, 1989), the assignment of tephras found in the VC-1 core to ones observed in outcrops was made mainly by close examination of stratigraphic position and tephra texture (Self et al., 1991). Even the chemical and isotopic composition of the glasses and phenocrysts do not uniquely identify the different units of the Valles Rhyolite (Gardner et al., 1986; Vuataz et al., 1988,; Wolff and Gardner, 1995). The main differences in interpretations for the assignment reviewed above are as follows: (1) whether the crystal-lithic nonwelded to welded tuff between 149 and 161 m in hole VC-1 is BSR (Goff and Gardner, 1987) or part of BBO (Self et al., 1991); (2) whether the tuff of various textures between 181 and 298 m is BSR (Self et al., 1991) or a distinct new unit named VC-1 Tuff (Goff and Gardner, 1987); and (3) whether the lithic-rich welded tuff between 293 and 298 m is EC (Self et al., 1991) or part of the VC-1 Tuff (Goff and Gardner, 1987).

ESR detects unpaired electrons associated with lattice defects or impurities. Even if major chemical composition and trace element compositions are not distinctive, ESR may distinguish the difference in impurity concentrations in quartz. Identical major and trace chemical compositions of the units of the Valles Rhyolite would indicate that those rhyolite magmas were closely related because these units would have evolved from the same magma system that postdates the larger Bandelier magma system. However, it would be still possible for those magmas to capture quartz grains from different sources at eruption. If this is the case, it may be possible to determine the origin of quartz grains by comparing them with quartz grains of possible source rocks.

Three types of Ti centers in quartz

In this investigation, we examined ESR signals of Ti centers, of which there are three types. When a Ti ion replacing a Si traps an electron created by natural radiation, it also traps a cation in order to compensate the charge (Weil, 1984). There are three candidates, Li^+, H^+, and Na^+ in quartz. After trapping one of these cations, Ti centers show distinct ESR signals. The g values (corresponding to the magnetic field where the signal appears) of the Ti-Li center are 1.979, 1.931, and 1.912, with four hyperfine lines due to $^7Li^+$ ($I = 3/2$, 92.5%) whereas g values of the Ti-H center are 1.986, 1.915, and 1.931, with two hyperfine lines due to $^1H^+$ ($I = 1/2$, 99.99%). The g values of the Ti-Na center are 1.968, 1.954, and 1.899, with four hyperfine lines due to $^{23}Na^+$ ($I = 3/2$, 100%) (Okada et al., 1971; Rinneberg and Weil, 1972; Isoya et al., 1983; Toyoda, 1992, fig. 2-1d).

Samples

ESR signals were obtained from nine quartz samples, four of which (BSR, EC, BBO, SMR) were collected in outcrops (Fig. 1) and five of which were from the VC-1 core at depths between 152.6-152.9 m (BVC-1), 162.5-162.8 m (VC-1R, VC-1 Rhyolite), 185.9-187.8 m (UVC-1, upper part of debated tuff), 216.1-217.6 m (MVC-1, middle part of debated tuff), and 295.1-295.4 m (LVC-1, the bottom part of the debated tuff). These quartz grains are xenocrystic because they tend to be partially resorbed and often have clinopyroxene reaction rims, indicating that the quartz is out of equilibrium with the host rhyolite melt (Gardner et al., 1986).

Results and discussion

About 100 mg of each quartz sample was measured at liquid nitrogen temperature (77° K). A spectrum showing three types of Ti center signals was obtained for EC02 (Fig. 2). The major contribution to the observed ESR signals of the other samples (Fig. 3) is from the Ti-Li center signals. The signals due to the Ti-H center are recognized by the two hyperfine line peaks centred at $g = 1.986$ and the lower dip of two hyperfine lines centered at $g = 1.915$, but expected structures around $g = 1.931$ overlap with the Ti-Li signals.

As summarized in Table 1, BBO (Fig. 3a) and SMR (Fig. 3g) showed Ti-Li signals but no Ti-H signal, whereas all other samples showed both signals. The intensity of the Ti-Li center signal in SMR was four to six times higher than that in other samples, presumably because of its greater age. The signal intensities in the samples from the VC-1 core were smaller than those from outcrops because higher present temperatures (up to 60°C) have partially annealed the signals.

Each of the samples of three members of the youngest Valles Rhyolite taken from outcrops shows a distinctive ESR signal pattern. BBO (Fig.

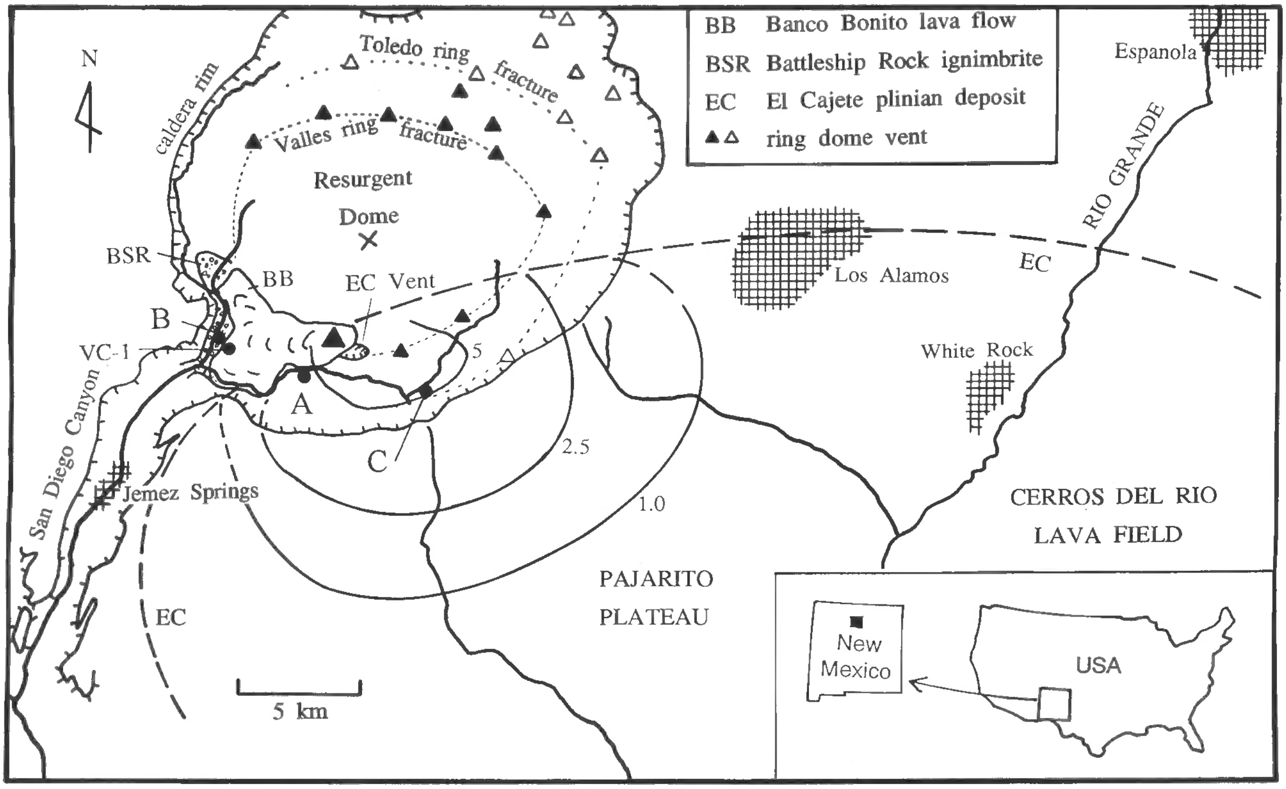

FIGURE 1. Localities of samples collected for the present ESR investigations. EC02 (El Cajete Pumice fall) and 90-7 (Banco Bonito Obsidian lava flow) were collected at site A; BSR04 (Battleship Rock ignimbrite) at site B; SMR01 (South Mountain Rhyolite) at site C. Samples BVC-1 (152.6–152.9 m), VC-1R (162.5–162.8 m, VC-1 Rhyolite), UVC-1 (185.9–187.8 m, VC-1 Tuff), MVC-1 (216.1–217.6 m, VC-1 Tuff) and LVC-1 (295.1–295.4 m) were from VC-1 core. Isopach of El Cajete pumice fall deposit are shown in meters. This figure is partially modified after Self et al. (1988).

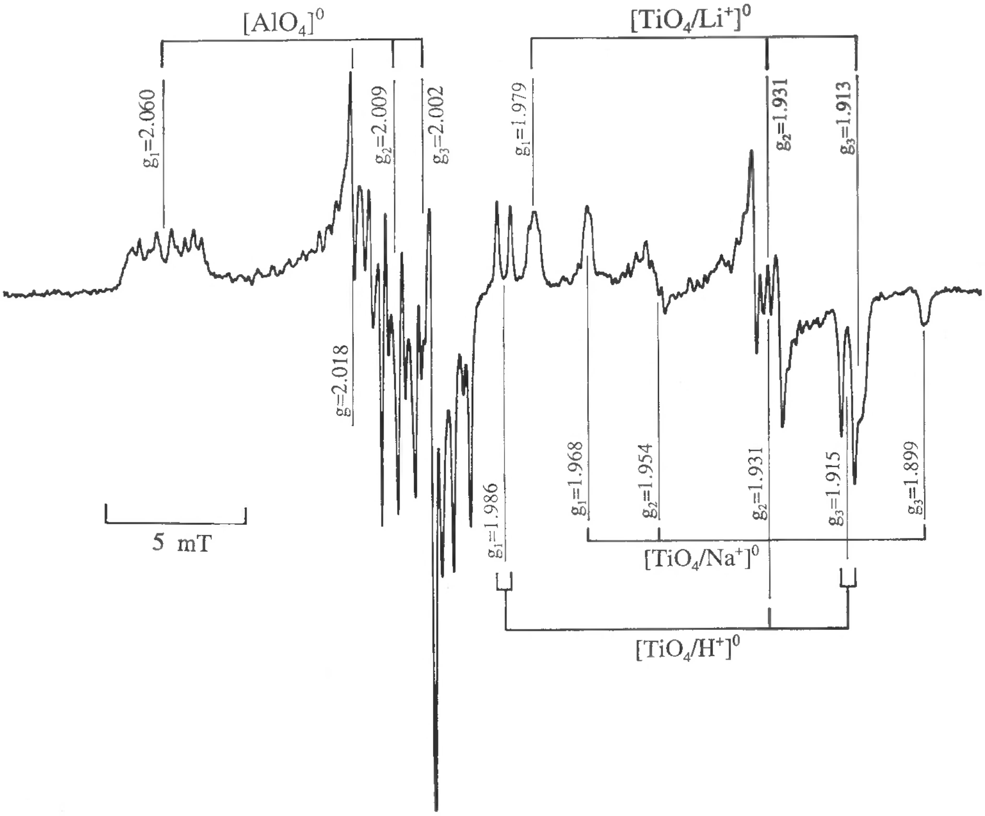

FIGURE 2. Typical ESR signals observed in natural quartz at liquid nitrogen temperature (77° K) obtained by using a ESR spectrometer, JEOL, RE-1X.. All three types of Ti centers (Ti-Li, Ti-H, and Ti-Na) were observed in EC02 (El Cajete Member) as shown in this figure. Spectrometer settings: microwave power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 0.1 mT; scan width, 40 mT; scan time, 8 min; time constant, 0.3 seconds.

3a) has only the Ti-Li signals, whereas BSR (Fig. 3b) has the Ti-Li center signals with a small intensity of Ti-H center signals. EC has all three types (Ti-Li, Ti-H, and Ti-Na, Fig. 2) with the intensity of Ti-H center (the height from the baseline to the bottom of the dip at the lower field of the hyperfine lines centered at g = 1.915) larger than that of the Ti-Li center (the height from the baseline to the bottom of the dip at g = 1.913).

The quartz signals in VC-1 Rhyolite (VC-1R, Fig. 3c) are identical to those in BSR (Fig. 3b), implying the same source of quartz grains. In addition, when the samples are irradiated by γ rays, the slopes in the signal responses to irradiation dose coincide completely with each other (Fig. 4). If these two units are closely related, the age of the VC-1 Rhyolite is much younger than the scattered ages obtained by ^{40}Ar-^{39}Ar method (Spell and Harrison, 1993) and is probably close to the age of BSR, which is about 60 ka (Toyoda et al., 1995).

TABLE 1. A score sheet for the Ti center signals observed in the present samples. +, observed; –, not observed; ++ (Ti-H): the peak height from the baseline to the bottom of the one at the higher field of hyperfine lines at g = 1.915 is larger than the height at g = 1.913, due to Ti-Li center.

Sample	Member	Type	Depth in the core (m)	Ti-Li	Ti-H	Ti-Na
90-7	BBO	outcrop	—	+	-	-
EC02	EC	outcrop	—	+	++	+
BSR04	BSR	outcrop	—	+	+	-
BVC-1		VC-1 core	152.6-152.9	+	+	-
VC-1R	VC-1 Rhyolite	VC-1 core	162.5-162.8	+	+	-
UVC-1	VC-1 Tuff	VC-1 core	185.9-187.8	+	+	-
MVC-1	VC-1 Tuff	VC-1 core	216.1-217.6			
LVC-1	VC-1 Tuff	VC-1 core	295.1-295.4	+	+	-
SMR01	SMR	outcrop	—	+	-	-

The signals in sample UVC-1 (Fig. 3d) and MVC-1 (Fig. 3e) are identical and also apparently similar to those of BSR. However, the intensity of the Ti-H center in these two samples, compared with that of the Ti-Li center, would be relatively larger than that in BSR as the lower field dip of the hyperfine lines centered at g = 1.915 is clearly shown in UVC-1 and MVC-1 (Fig. 3d, e, whereas no dip is recognized in BSR (Fig. 3b). When the dose response of the Ti-Li and the Ti-H signals in these samples were examined together with BSR, the slopes for UVC-1 and MVC-1 were the same but different from the slope for BSR (Fig. 4). We believe that VC-1 Tuff is a unit different from BSR. The precise results on the dose responses will be published separately.

LVC-1 (Fig. 3f), which is of a unit assigned to EC by Self et al. (1991), showed Ti-Li and small Ti-H signals but no Ti-Na signal; EC showed all three signals. The signals possibly result from a mixture of several tephras of different origins because this unit includes many lithic fragments. If this unit contains fragments of EC pumice, the ESR signals should have the feature of the signals of the EC outcrop sample, possibly with smaller intensities. The fact that LVC-1 did not show a Ti-Na signal would indicate that this unit is not related to EC. As shown in Figure 3f, the feature is rather similar to that of the VC-1 Tuff (Fig. 3d, e) where hyperfine line peaks centered at g = 1.986 are relatively large and the lower field dip of the hyperfine lines centered at g = 1.915 is also shown.

BVC-1 quartz shows one of the Ti-Li center signals with one of the Ti-H signals (Fig. 3h) although only a part of the spectrum has been obtained so far. The Ti-H signal is recognized from the lower field dip of the hyperfine lines centered at g = 1.915. The absence of this feature in BBO (Fig. 3a) indicates that the assignment of this part of the core to BBO made by Self et al. (1991) is incorrect. However, it appears that the feature is also different from that of BSR because this dip is not recognizable in BSR (Fig. 2b). This point would need to be clarified further by measurements with higher signal to noise ratios. It is still possible that BVC-1 is from BSR because such a feature, having both Ti-Li and Ti-H center signals, is that of BSR.

The results and discussions above are summarized as follows. ESR

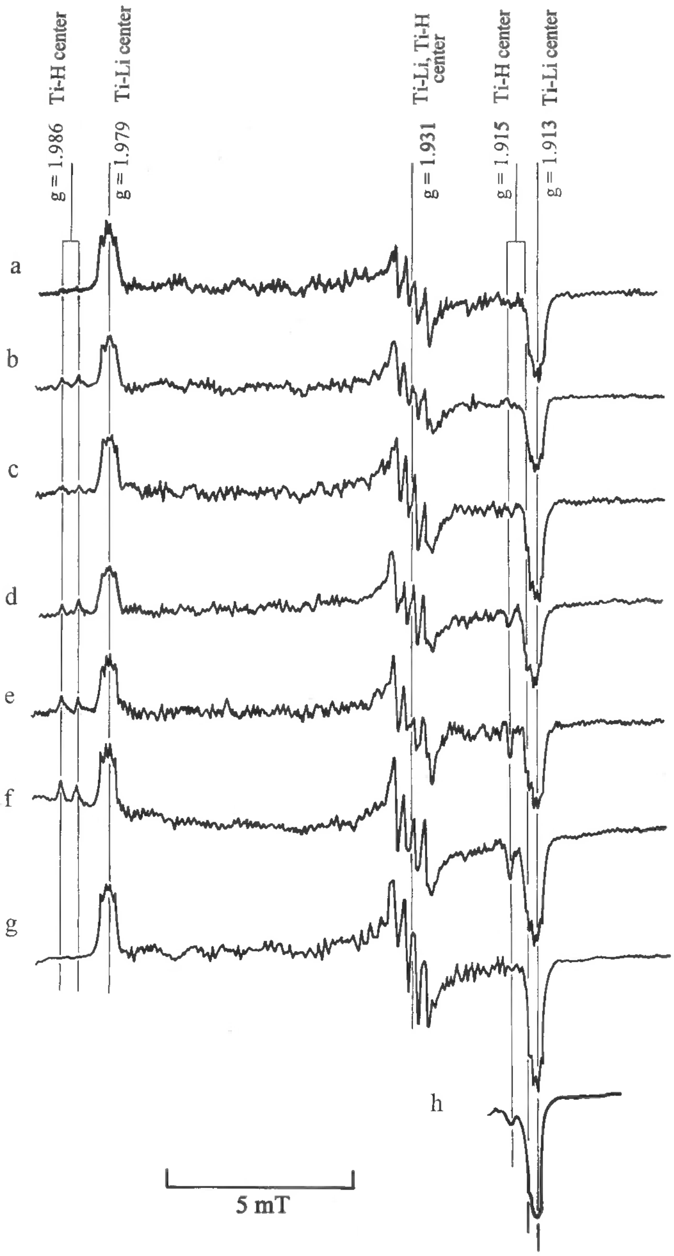

FIGURE 3. Ti center signals observed in the present samples by using an ESR spectrometer, Bruker, ER100D, except for EC02 (see Fig. 2). a, 90-7 (Banco Bonito Member); b, BSR04 (Battleship Rock Member); c, VC-1R (VC-1 Rhyolite); d, UVC-1 (VC-1 Tuff); e, MVC-1 (VC-1 Tuff); f, LVC-1; g, SMR01 (South Mountain Rhyolite); h, BVC-1. The Ti-Li center signals are observed in all samples, whereas the Ti-H signals are not observed in a and g. Ti-Na signals are observed only in EC02 (Fig. 2). Spectrometer settings except for h, microwave power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 0.1 mT; scan width, 20 mT; scan time, 500 seconds; time constant, 0.5 seconds. The settings for h: the same as that for Figure 2 except for the scan width of 20 mT. h was obtained by using JEOL, RE-1X.

signals in xenocrystic quartz from the rhyolites in VC-1 core samples indicate that (1) the tephra unit between depths of 150 and 160 m is not part of BBO, but probably BSR ignimbrite; (2) ESR signals in quartz from VC-1 Rhyolite lava are identical to those of BSR ignimbrite, implying a close genetic relationship between these two units; (3) the tephra units between depths 180 and 290 m are distinctive, and different from BSR ignimbrite; and (4) the tephra unit between depths of 290 and 300 m is not part of the EC deposits. The above indications generally support the stratigraphic assignments by Goff and Gardner (1987) rather than those by Self et al. (1991), as shown in Figure 5.

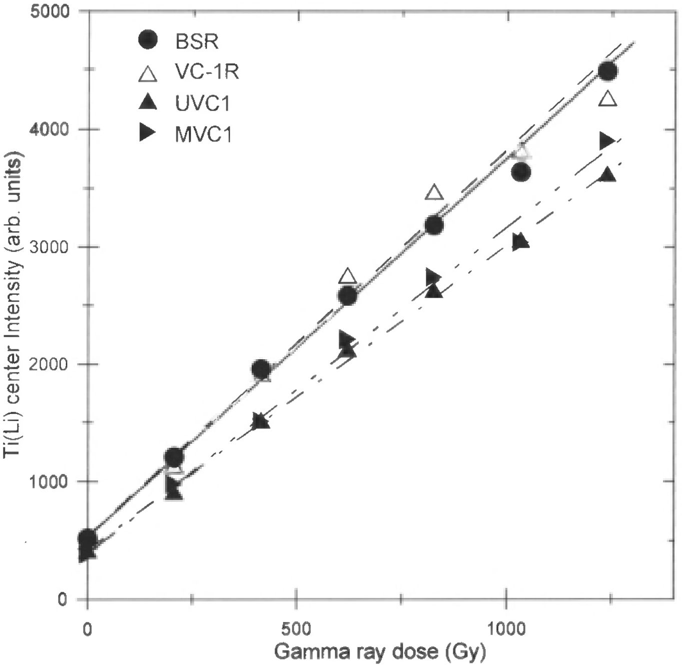

FIGURE 4. Enhancement of Ti-Li center signal by γ ray irradiation. The irradiation was performed by using the facility at Nara University of Education with a dose rate of 50 Gy/hr. BSR04 and VC-1R show identical signal intensities at all irradiation doses to UVC-1 and MVC-1 although the slope of each group is different from the other. The lines were fitted by the least square method to the points shown; the solid line for BSR, the broken line for VC-1R, the broken line with a dot for UVC-1, and the broken line with two dots for MVC-1.

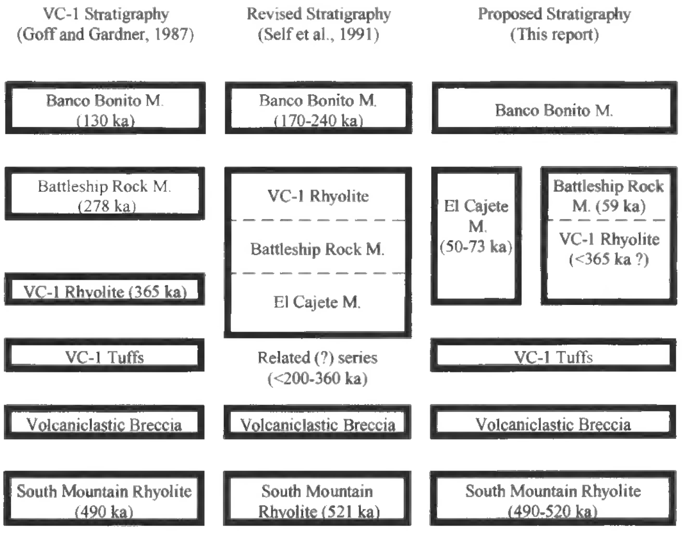

FIGURE 5. Chart showing the stratigraphic sequences proposed by Goff and Gardner (1987) and Self et al. (1991) in comparison with the one proposed in this work. The results of the present ESR investigation suggest that the Battleship Rock Member and VC-1 Rhyolite are closely related and that the VC-1 Tuff is a distinctive unit. However, the stratigraphic position of the El Cajete Member is not clear yet.

The origin of the quartz grains in these Valles Rhyolite samples was not elucidated by the present work. They could be from the underlying Precambrian basement, Paleozoic sandstones, Santa Fe Group sandstones, or quartz-bearing intrusive rocks of the Jemez volcanic field. Identification of their origin could be possible using this ESR technique if quartz grains from these rock units are examined.

CONCLUSIONS

ESR dating of minerals in volcanic rocks, including quartz phenocrysts or xenocrysts, is a viable method, particularly when several signals can be examined in detail. ESR studies can yield eruption ages even when contamination from basement rocks causes the serious excess ^{40}Ar problem because of the low thermal stabilities of the ESR signals. However, subsequent low-temperature thermal disturbance can affect the ESR signal intensities. It would be important, in such cases, to examine the thermal stabilities of the signal.

The patterns (or fingerprints) of ESR signals in minerals can help make stratigraphic assignments of volcanic units where traditional field and geochemical methods are not adequate. Although our ESR study on the youngest rhyolites in the southwestern moat of Valles caldera is preliminary, the results indicate that the El Cajete Pumice and Battleship Rock Ignimbrite erupted at about 55-60 ka. Thermal annealing due to young hydrothermal events inside the caldera has occurred during the past 10-40 ka. In addition, our work indicates that the stratigraphic assignments made by Goff and Gardner (1987) on units in the upper 300 m of the VC-1 core are probably correct. Although additional work is in progress, it is our present belief that the VC-1 Tuffs are unique from the Battleship Rock Ignimbrite.

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