ISSN 1819-7140, Russian Journal of Pacific Geology, 2013, Vol. 7, No. 3, pp. 212–216. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.V. Grebennikov, V.K. Popov, A.I. Khanchuk, 2013, published in Tikhookeanskaya Geologiya, 2013, Vol. 32, No. 3, pp. 80–85.

Experience of Petrochemical Typification of Acid Volcanic Rocks from Different Geodynamic Settings

A. V. Grebennikov, V. K. Popov, and A. I. Khanchuk

Far East Geological Institute, Far East Branch, Russian Academy of Sciences, pr. Stoletiya Vladivostoka 159, Vladivostok, 690022 Russia

e-mail: greandr@hotmail.com

Received November 16, 2012

Abstract—A classification diagram was empirically developed for acid volcanic rocks formed in modern geodynamic settings and reflects their peculiar chemical features. The testing of the binary diagram Al_2O_3/(CaO + MgO) – $Fe_2O_3^{Tot}$/(CaO + MgO) for the Late Cretaceous (Pimorsky, Siyanovsky, Kamensky, and Levosobolevsky) and Paleogene (Bogopolsky) Volcanic Complexes of East Sikhote Alin demonstrated its high efficiency for deciphering the tectonic settings of ancient acid volcanism.

Keywords: geochemical classification, geodynamic settings, petrogenic elements, rhyolites

DOI: 10.1134/S1819714013030044

INTRODUCTION

A great number of diagnostic (discriminant) diagrams have been developed on the basis of the geochemical composition of acid magmatic rocks for deciphering the geodynamic settings of magmatism. The most frequently applied classification diagrams (Pearce et al., 1984; Batchellor and Bowden, 1985; Harris et al., 1986; Whalen et al., 1987; Maniar and Piccoli, 1989; Velikoslavinsky, 2003; and others) were constructed exclusively for granitic rocks. The chemical identity of intrusive and volcanic rocks formed in subduction and within-plate settings was demonstrated only in [2]. However, special studies of the validity of these diagrams for volcanic analogues (dacites and rhyolites) have not been conducted yet. Some reseachers [7] demonstrated that the application of these diagrams to acid volcanic rocks may lead to invalid conclusions. We encountered this problem during the study of Late Cretaceous and Paleogene ignimbrites of East Sikhote Alin [14]. Thus, a search for reliable geodynamic interpretations of petrogeochemcial data on acid volcanic rocks has remained an urgent problem. The main problem in the systematics of acid magmatic rocks consists in the variability and convergence of the petrogeochemical composition due to their polygenous origin and intense chemical interaction with other rocks (and melts). Finally, this may lead to the obliteration of the petrochemical signatures of acid volcanic rocks of different geodynamic settings.

STUDY RESULTS

According to the tectonic and geochemical (for basalts) reconstructions of the Mesozoic–Cenozoic evolution of the Asian continental margin, the Late Cretaceous volcanic rocks were formed during subduction, while the Paleogene rocks were derived in a transform plate margin setting [16, 18]. Previous works on the geochemical typification of Late Cretaceous and Paleogene acid volcanic rocks from East Sikhote Alin (using the aforementioned diagnostic diagrams for granitic rocks) led to ambiguous results [4]. In most geochemical discriminant diagrams, the data points of the volcanic complexes of different ages occupy uncertain positions, plotting simultaneously in the fields of the island- and continental volcanic arc granitoids, as well as in the field of collisional and within-plate granitoids. In this relation, we attempted to construct discriminant petrochemical diagrams for the acid volcanic rocks. In particular, the fields of Late Cretaceous and Paleogene ignimbrites of East Sikhote Alin are well distinguished in the diagrams (CaO + MgO)–(K_2O + Na_2O) and (CaO + MgO)–(FeO + Fe_2O_3) (Fig. 1). However, deciphering the geodynamic settings of the ancient acid volcanism can be solved only on the basis of generalization of the data on similar rocks formed in modern suprasubduction, plate sliding (transform plate margin), within-plate, and spreading settings. The volcanism of collisional zones was generated by the sliding of the lithospheric plates during and after their collision.

The detection of petrochemical parameters was caused by the behavior of the trace elements in the acid melts. We agree with the conclusions in [29] that

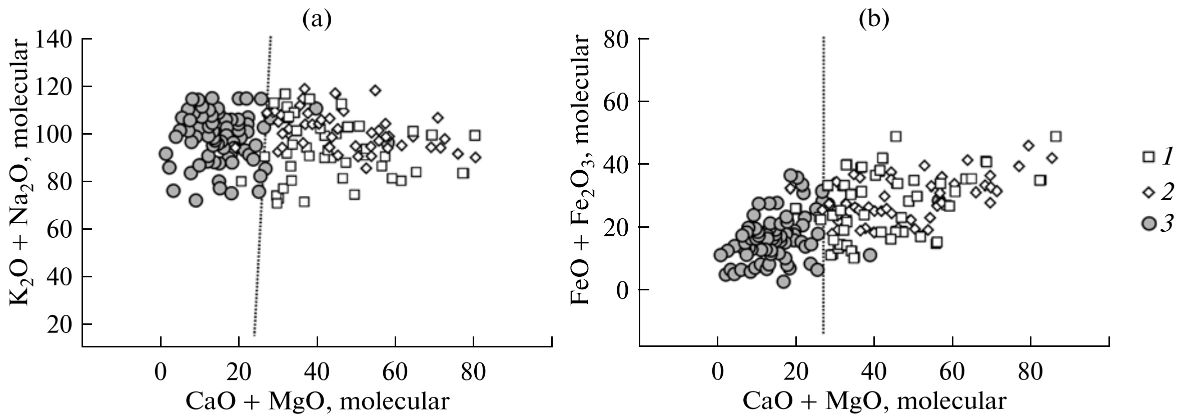

Fig. 1. Diagrams: (a) $(Na_2O + K_2O)-(CaO + MgO)$ (molecular); (b) $(Fe_2O_3 + FeO)-(CaO + MgO)$ (molecular).
Data points of acid volcanic rocks: (*1*) Turonian–Santonian Primorskaya Unit; (*2*) Campanian–Maastrichtian Siyanovsky, Kamensky, and Levosobolevsky Volcanic Complexes; (*3*) Paleocene–Eocene Bogopolsky Volcanic Complex.

the existing geochemical classifications of granitic rocks based on trace- and minor-element abundances cannot unambiguously identify the magmatic source or tectonic setting. Minor elements in acid melts, unlike those in basalts, usually reveal incompatible behavior [25]. REE, U, Th, and Zr are usually incorporated in such accessory minerals as apatite, zircon, titanite, orthite, and monazite, while Nb and Y are accumulated in oxides and amphiboles. Correspondingly, their contents are determined by the crystallization as a function of the extensive parameters (oxygen and water fugacity). Crustal contamination affects the concentrations of trace elements to a greater extent than those of petrogenic oxides. Thus, the use of minor elements and their ratios as factors of the classification of granitic rocks often cannot provide unambiguous identification of the magmatic source or geodynamic setting.

Diagrams were constructed on the basis of 600 published chemical analyses of diverse-facies acid volcanic rocks (tuffs, ignimbrites, lavas, and extrusive bodies) formed in different geodynamic settings. The data set included only acid volcanic rocks ($SiO_2 > 67$ wt %) unaltered by secondary processes with L.O.I. < 4 wt %. Rocks representing fragments of glasses, fiamme, and end members of highly differentiated melts and liquid immiscibility products were omitted. The composition was calculated to 100% water free. The molecular amounts were calculated using the standard techniques [20].

Numerous triangle and binary petrochemical diagrams were empirically compiled to obtain the most informative $Al_2O_3/(CaO + MgO) - Fe_2O_3^{Tot}/(CaO + MgO)$ diagram (Fig. 2). In our opinion, the proportions of Al, Fe, and sum of thermophile cations (Ca and Mg) may serve as the major petrochemical criteria for distinguishing between the rocks of different geodynamic settings. As is seen in the presented diagram, the data points of the rocks with insignificant overlapping define four main fields. The first field (I) includes volcanic rocks related to island-arc and continental–margin suprasubduction magmatism. They include dacites and rhyolites from the Cascades (USA) [33], ignimbrites from the volcanic front of the Andean belt (Argentina, Bolivia, and Chile) [10, 28, 39, 40, 42], and ignimbrites of Kamchatka (the Uzon and Semyachik Volcanoes) [9]. The second field (II) comprises volcanic rocks from intra- and continental transform-plate margins. They are represented by rhyolites of extrusive domes and lava piles of Californian-type Coso province in California in the United States [22], as well as by rhyolites from the western coast of America (about 30 manifestations in Nevada, Utah, and Idaho in the United States) [27] and the Yellowstone supercaldera (Wyoming, USA) [26, 31, 41]. The third field (III) encloses data on the within-plate alkaline rocks, in particular, ignimbrites from the East African rift system [38, 43], as well as pantellerites and comendites from the Paektusan Volcano (Korea–China boundary) [13], acid volcanic glasses and breccias from the Kergelen plateau (Indian Ocean) [24, 37], rhyolitic domes of the Red Sea [21], and rhyolites of oceanic islands (Easter, Socorro, Ascension, Bouvet, and others) [23, 36]. The fourth field (IV) is formed by acid volcanics from spreading zones: rhyolites from the Alcedo Volcano (Galapagos Islands) [30] and Iceland [6, 34, 35]. Thus, distinguished fields I–IV correspond to the composition of the acid volcanic rocks of modern geodynamic settings.

The next step involved plotting the data points of the Late Cretaceous ignimbrites of the Siyanovsky, Levosobolevsky, Kamensky, and Primorsky Complexes and the Paleogene ignimbrites of the Bogopolsky Complex (East Sikhote Alin) in the diagram. The data set included our original [5, 32] and literature [1, 3, 8, 11, 12, 15, 19] data, as well as materials from geological reports. In the developed diagram (Fig. 2), the

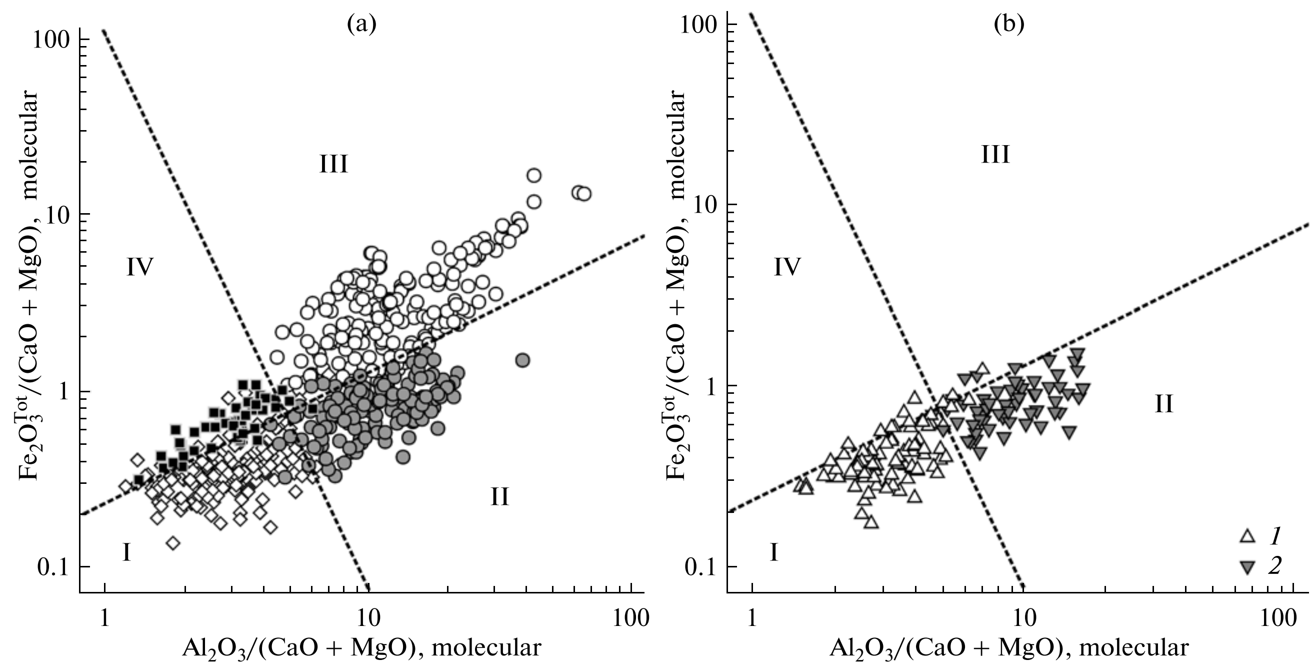

Fig. 2. Diagrams: (a, b) $Al_2O_3/(CaO + MgO)–Fe_2O_3^{tot}/(CaO + MgO)$ (molecular).

Fields I–IV are separated by lines taking their origin at the points with the following coordinates: (a) 1–0.5, 1000–60; 10–0.1; 10–100; (b) 1–0.22, 100–7; 1–100; 9–0.1.

(I) Zones of island-arc and continental-margin suprasubduction magmatism: rhyolites of Kamchatka (the Uzon and Semyachik Volcanoes); Andean rhyolites (Chile, Bolivia, Argentina); rhyolites of the Cascades (northwestern USA). (II) Zone of transform plate boundarys: within- and marginal continental types: rhyolites of extrusive domes and lava flows (California, USA); Topaz rhylites from the western coast of North America (Idaho, Utah, and Nevada, USA): Yellowstone rhyolites (Western USA); (III) Zones of within-plate magmatism of oceanic and continental types: rhyolites of Kergelen Island (Indian Ocean); alkaline rhyolites from the Paektusan Volcano; alkaline rhyolites of the East African rift system; rhyolites of the Red Sea (Egypt); rhyolites of oceanic islands; (IV) spreading zones: rhyolites of the Galapagos Islands; rhyolites of Iceland.

Symbols in Fig. 2b: (*1*) rhyolites of the East Sikhote Alin volcanic belt (the Primorsky, Siyanovsky, Kamensky, and Levosobolevsky Volcanic Complexes); (*2*) rhyolites of the Bogopolsky Complex, Primorye.

data points of the Late Cretaceous volcanics fall in the suprasubduction field (Field I), while the Paleogene ignimbrites, in the field of transform-plate margin settings (Field II) (Fig. 2c). The obtained data more reliably supported the previous conclusions reached for basalts [16, 28] than the manifestations of Late Cretaceous and Paleogene magmatism formed on the Asian continental margin. These conclusions are confirmed by geological and petrological studies of the acid volcanism of East Sikhote Alin on the Late Mesozoic–Early Cenozoic boundary [3–5, 15, etc.].

The Turonian–Campanian volcanic rocks of the Primorskaya Unit compose a linear structure of the East Sikhote Alin volcanic belt. They are represented by crystal-rich plateau ignimbrites of S-type rhyolites, rhyodacites, and dacites formed due to high-volume fissure eruptions of acid magmas [14]. They were generated in an oxidizing setting with the participation of aqueous fluids typical of suprasubduction volcanism. In the Campanian–Maastrichtian, the volcanic centers were localized within depression-type volcanotectonic structures superimposed onto the plateau ignimbrite fields of the volcanic belt. This period was marked by bimodal magmatism. The products of the acid volcanism distinguished in the Kamensky, Levosobolevsky, and Siyanovsky Complexes are represented by dacite–rhyolite tuffs and ignimbrites, while the Samarga and Dorofeevsky Complexes are made up of basalts, andesites, and dacites. The caldera-type acid volcanics of this period were geochemically similar to the S-type plateau ignimbrites of the Primorskaya Unit. The rocks of the Paleocene–Early Eocene explosive acid volcanism of the Bogopolsky Complex fill collapsed calderas, being represented by tuffs, hyaloignimbrites, and subvolcanic bodies of vitrophyric dacites and rhyolites formed owing to the eruption of S-type peraluminous acid magmas (at the initial stage) and Fe-rich A-type melts (at the final stages). The A-type high-Fe hyaloignimbrites of the Bogopolsky Complex bear well expressed mineralogical and geochemical signatures of the interaction between crustal magmas and the enriched sublithospheric mantle. Their formation was presumably assisted by reduced (essentially hydrogen) fluids [32] derived from the enriched asthenosphere during the formation of acid crustal magmas. These signatures are typical of extensional mantle and crustal magmatism produced on a transform continental margin [17].

CONCLUSION

In this work, we reported the first results of the empirical construction of discriminant diagram for acid volcanic rocks, which confirms the chemical peculiarity of the acid volcanic rocks formed in subduction, within-plate, spreading, and transform plate boundary settings. The first verification of this diagram for the Late Cretaceous and Paleogene volcanics demonstrated its applicability to tectonic reconstructions.

ACKNOWLEDGMENTS

We are grateful to N.A. Goryachev (Northeast Interdisciplinary Research Institute, Far East Branch, Russian Academy of Sciences, Magadan) for useful comments that significantly improved this work. Ya.V. Kuz'min (Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences) is thanked for help in obtaining access to international journals, while N.V. Zarubina (Far East Geological Institute, Far East Branch, Russian Academy of Sciences, Vladivostok) for fruitful consultations concerning the recalculations of the chemical analyses of rocks.

This work was supported by the Far East Branch of the Russian Academy of Sciences (projects nos. 12-III-A-08-155 and 12-1-0-ONZ-07).

Recommended for publishing by N.A. Goryachev

REFERENCES

1. V. A. Baskina, *Magmatism of Ore-Controlling Structures of Primorye* (Nauka, Moscow, 1982) [in Russian].
2. S. D. Velikoslavinskii, "Geochemical classification of silicic igneous rocks of major geodynamic environments," Petrology **11** (4), 327–342 (2003).
3. V. V. Vetrennikov, *Features of Volcanism, Tectonics, and Mineralization of Marginal-Sea Volcanic Belts* (Nedra, Moscow, 1976) [in Russian].
4. *Geodynamic, Magmatism, and Metallogeny of East Russia,* Ed. by A. I. Khanchuk (Dal'nauka, Vladivostok, 2006) [in Russian].
5. A. V. Grebennikov, Extended Abstracts of Candidate's Dissertation in Geology and Mineralogy (Vladivostok, 2003).
6. *Iceland and Mid-Oceanic Ridge. Geochemistry* (Nauka, Moscow, 1978), p. 183 [in Russian].
7. N. V. Koronovsky and L. I. Demina, *Magmatism as Indicator of Geodynamic Settings. A Tutorial* (Mosk. Gos. Univ., Moscow, 2011) [in Russian].
8. A. M. Kurchavov, *Lateral Variability of Volcanic rocks: Evidence from South Primorye* (Nauka, Moscow, 1979) [in Russian].
9. V. L. Leonov and E. N. Grib, *Structural Position and Volcanism of Quaternary Calderas of Kamchatka* (Dal'nauka, Vladivostok, 2004) [in Russian].
10. *Magmatic Rocks. vol. 4. Acid and Intermediate Rocks,* Ed. by V. V. Yarmolyuk and V. I. Kovalenko (Nauka, Moscow, 1987) [in Russian].
11. L. F. Mishin, "Eutectoid and cotectoid petrographic types of acid volcanic and subvolcanic rocks of the continental margin volcanic belts as exemplified by East Asia," Russ. J. Pac. Geol. **29** (2), 69–85 (2009).
12. V. A. Mikhailov, *Magmatism of Volcanotectonic Structures of the Southern Part of the Eastern Sikhote Alin Volcanic Belt* (Vladivostok, 1989) [in Russian].
13. V. K. Popov, V. G. Sakhno, Ya. V. Kuz'min, et al., "Geochemistry of volcanic glasses from the Paektusan Volcano," Dokl. Earth Sci. **403** (2), 803–807 (2005).
14. V. K. Popov and A. V. Grebennikov, Geochemical features of the Late Cretaceous and Paleogene ignimbrite volcanism of eastern Sikhote Alin as indicators of a change of geodynamic regime on the Mesozoic–Cenozoic boundary, in *Proceedings of All-Russian Conference "Geological Processes in Settings of Subduction, Collision, and Transform-Plate Margin", Vladivostok, Russia, 2011* (Dal'nauka, Vladivostok, 2011) [in Russian].
15. V. G. Sakhno, *Late Mesozoic–Cenozoic Continental Volcanism of East Asia* (Dal'nauka, Vladivostok, 2001) [in Russian].
16. A. I. Khanchuk, V. V. Golozubov, Yu. A. Martynov, et al., "Early Cretaceous and Paleogene Californian-type transform continental margins of the Russian Far East," in *Tectonics of Asia* (GEOS, Moscow, 1997), pp. 240–243 [in Russian].
17. A. I. Khanchuk, Yu. A. Martynov, A. B. Perepelov, and N. N. Kruk, "Magmatism of lithospheric plate sliding zones: new data and prospects," in *Proceedings of 4th All-Russian Symposium on Volcanology and Paleovolcanology, Petropavlovsk-Kamchatskii, Russia, 2009* (Petropavlovsk-Kamchatskii, 2009), Vol. 1, pp. 32–37 [in Russian].
18. A. I. Khanchuk and Yu. A. Martynov, "Tectonics and magmatism of the sliding of oceanic and continental plate margins," in *Proceedings of All-Russian Conference "Geological Processes in Settings of Subduction, Collision, and Transform Plate Margins, Vladivostok, Russia"* (Dal'nauka, Vladivostok, 2011), pp. 45–49 [in Russian].
19. I. Yu. Chekryzhov, V. K. Popov, A. M. Panichev, et al., "New data on the stratigraphy, volcanism, and zeolite mineralization of the Cenozoic Vanchinskaya depression in Primorye," Russ. J. Pac. Geol. **29** (3), 45–63 (2010).
20. S. D. Chetverikov, *A Handbook to Petrochemical Recalculations of Chemical Analyses of Rocks and Determination of Their Chemical Types* (Gosgeoltekhizdat, Moscow, 1956) [in Russian].
21. M. K. Azer, "Tectonic significance of Late Precambrian calcalkaline and alkaline magmatism in Saint Katherina area, southern Sinai, Egypt," Geologica Acta **5**, 255–272 (2007).
22. C. R. Bacon, R. MacDonald, R. L. Smith, and P. A. Baedecker, "Pleistocene high-silica rhyolites of

the Coso volcanic field, Inyo County, California," J. Geophys. Res. **86**, 10223–10241 (1984).

23. P. E. Baker, "Peralkaline acid volcanic rocks of oceanic islands," Bull. Volcanol. **38**, 737–754 (1974).
24. J. Barron, B. Larsen, J. Baldauf, and Shipboard Scientific Party [M.J. Hambrey; 30 authors], Proc. OCDP **119**, (1991).
25. F. Bea, "Residence of REE, Y, Th, and U in granites and crustal protoliths, implications for the chemistry of crustal melts," J. Petrol. **37**, 521–552 (1996).
26. H. E. Cathey and B. P. Nash, "The Cougar Point tuff: implications for thermochemical zonation and longevity of high-temperature, large-volume silicic magmas of the Miocene Yellowstone hotspot," J. Petrol. **45**, 27–58 (2004).
27. E. H. Christiansen, I. Haapala, and G. L. Hart, "Are Cenozoic Topaz rhyolites the erupted equivalents of Proterozoic rapakivi granites? Examples from the eestern United States and Finland," Lithos **97**, 219–246 (2007).
28. B. Coira and S. M. Kay, "Implications of Quaternary volcanism at Cerro Tuzgle for crustal and mantle evolution of the Puna Plateau, Central Andes, Argentina," Contrib. Mineral. Petrol. **113**, 40–58 (1993).
29. B. R. Frost, C. G. Barnes, W. J. Collins, et al., "A geochemical classification for granitic rocks," J. Petrol. **42**, 1771–1802 (2001).
30. D. Geist, K. A. Howard, and P. Larson, "The generation of oceanic rhyolites by crystal gractionation: the basalt–rhyolite association at volcano Alcedo, Galapagos archipelago," J. Petrol **36** (4), 965–982 (1995).
31. G. Girard and J. Stix, "Rapid extraction of discrete magma batches from a large differentiating magma chamber: the Central Plateau Member rhyolites, Yellowstone Caldera, Wyoming," Contrib. Mineral. Petrol. **160**, 441–465 (2010).
32. A. V. Grebennikov and S. O. Maksimov, "Fayalite rhyolites and a zoned magma chamber of the Paleocene Yakutinskaya volcanic depression in Primorye, Russia," J. Mineral. Petrol. Sci. **101**, 69–88 (2006).
33. W. Hildreth, M. A. Lanphere, D. E. Champion, and J. Fierstein, Rhyodacites of Kulshan caldera, North Cascades of Washington: postcaldera lavas that span the Jaramillo, J. Volcanol. Geotherm. Res. **130**, 227–264 (2004).
34. K. Jonasson, P. M. Holm, and A. K. Pedersen, "Petrogenesis of silicic rocks from the Krysfjrdur central volcano, NW Iceland," J. Petrol. **33** (6), 1345–1369 (1992).
35. K. Jonasson, "Rhyolite volcanism in the Krafla central volcano, North-East Iceland," Bull. Volcanol. **56**, 516–528 (1994).
36. M. Karsten, P. E. Baker, and Fl. Buckley, "Petrology and geochemistry of Easter Island," Contrib. Mineral. Petrol. **44**, 85–100 (1974).
37. B. Kieffer, N. T. Arnd, and D. Weis, "A bimodal alkalic shield volcano on Skiff Bank: its place in the evolution of the Kerguelen Plateau," J. Petrol. **43**, 1259–1286 (2002).
38. R. M. MacDonald, G. R. Davies, and C. M. Bliss, et al., "Geochemistry of high-silica peralkaline rhyolites, Naivasha, Kenya Rift Valley," J. Petrol. **28**, 979–1008 (1987).
39. D. C. Noble, T. A. Vogel, P. S. Peterson, et al., "Rare-element enriched S-type ash-flow tuffs containing phenocrysts of muscovite, andalusite and sillimanite, southeastern Peru," Geology **1**, 35–39 (1984).
40. H. Pichler and W. Zeil, "The Cenozoic rhyolite–andesite association of the Chilean Andes," Bull. Volcanol. **35**, 424–452 (1971).
41. C. J. Pritchard and P. B. Larson, "Genesis of the post-caldera eastern Upper Basin Member rhyolites, Yellowstone, WY: from volcanic stratigraphy, geochemistry, and radiogenic isotope modeling," Contrib. Mineral. Petrol. **164**, 205–228 (2012).
42. S. Silva and P. W. Francis, "Correlation of large ignimbrites—two case studies from the Central Andes of Northern Chile," J. Volcanol. Geotherm. Res. **37**, 133–149 (1989).
43. T. Trua, C. Deniel, and R. Mazzuoliet, "Crustal control in the genesis of Plio-Quaternary bimodal magmatism of the Main Ethiopian Rift (MER): geochemical and isotopic (Sr, Nd, Pb) evidence," Chem. Geol. **155**, 201–231 (1999).

Translated by M. Bogina