Role of the Energy of Interface Formation in the Melting and Retrograde Boiling

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Abstract—The energy of interface formation is an important parameter that controls the evolution of magmatic systems. The energy factor plays a critical role during phase transitions at the beginning of crystallization, melting, and retrograde boiling, when numerous nuclei of one phase are formed within another phase. It was shown that the melting style significantly depends on geodynamics. In "static" conditions (oceanic spreading or intraplate activity), magma generation mainly occurs by propagation of melting zones due to decompression in the ascending plume. Newly formed melts migrate upward in intergranular spaces, thus accumulating beneath the upper, cooler zone of the plume to form magma chambers. In dynamic conditions (subduction zones), the bulk periodic and rapid melting is often observed. The composition of volatiles dissolved in the melt plays an important role during retrograde boiling. If CO_2 predominates, which is typical of intraplate magmas, the boiling in shallow magma chambers produces foam extruded to form cinder cones. Occasionally, this process is accompanied by small explosions, forming scoria–pyroclastic and pyroclastic cones. Explosive eruptions typical of deep-seated volatile-rich kimberlite and lamproite magmas are related to the abrupt decrease of CO_2 solubility in the ascending magmas at 40–50 kbar. Subduction-related water-saturated magmas are characterized by bulk boiling at shallow depths, which is often accompanied by catastrophic explosions. This is related to the abrupt decrease of H_2O solubility in the intermediate–acid melts at 1–1.5 kbar. The contribution of other volatiles (CO_2, SO_3, etc.) is insignificant in this case.

INTRODUCTION

Physical mechanisms of magmatic processes and their technology are the least understood petrologic problems. How are magmas generated and accumulated to form magma chambers, how do intrusions crystallize, and why does magma degassing occasionally lead to catastrophic explosions? The phenomena related to interface formation are important in all these cases. It is known that the interface formation is an energy-consuming process [1, 2]. Therefore, it is particularly influential in the case of extensive formation of interfaces.

These phenomena frequently occur in natural magmatic systems, since the appearance of new interfaces is a necessary condition of their generation and evolution. They are particularly notable at the moment of phase transition during magma crystallization (solidification) and boiling and rock melting, when new phases form in large amounts. There are three main mechanisms of the interface formation in magmatic systems: (1) melt generation and segregation, (2) crystal nucleation and growth, and (3) nucleation and growth of gas bubbles.

All these processes can be initiated only when an energy barrier of new interface formation is overcome. Therefore, the process does not begin at the equilibrium temperature of the phase transition, but an additional energy pulse (trigger) is required, such as overheating for melting and undercooling for crystallization and retrograde boiling. In the latter case, the scale of the process can abruptly increase with catastrophic consequences. The formation of new phase nuclei is a spontaneous process, which violently develops after initiation, since it already occurs within the stability field of the new phase. Moreover, the formation of new phases occurs in a certain volume or zone, whose spatial boundaries are determined by the equilibrium temperature of the phase transition and the energy required for initiation of this transition.

All of these three micro-scale processes are the main components of macro-scale processes (solidification of magma bodies and generation of melting and degassing domains). Earlier, we considered the role of interface formation during solidification of magma bodies [3]. In contrast, melting is a poorly studied process, since its traces are rare in restite. For the same reason, the theoretical base for study of this process is also poorly developed and mostly consists only of general, mainly geochemical, considerations. The same is true for retrograde boiling, when the energy of gas bubble nucleation is critical, especially for development of catastrophic volcanic explosions.

Therefore, understanding the mechanisms of melting and degassing in natural magmatic systems will

allow one to significantly constrain speculations and develop more realistic models of these processes. We discuss these problems below using available geological and geochemical data, as well as the results of geophysical investigations in areas of active volcanism.

ROLE OF THE INTERFACE FORMATION DURING MELTING

Like crystallization [3], rock melting with magma generation can occur under both static and dynamic conditions. Static conditions are typical of decompression-driven melting within the mantle plume head and above the plume within the Earth's crust. Dynamic conditions occur in subduction zones, where melting takes place under compression in a mobile environment and results in abundant island-arc magmatism.

Melting under Static Conditions

Theoretically, melting is inverse to crystallization, but it has some specific features. It is known that the beginning of melting requires overheating, which provides the necessary driving force for the formation of the liquid phase [4] and new phase interfaces. Melting heat is spent for weakening and break-up of intermolecular bonds. Therefore, similarly to crystallization, melting begins at crystal surfaces, edges, and cracks, where uncompensated atomic–molecular bonds are concentrated. For the same reasons, unlike crystallization, melting primarily involves dislocation areas.

The study of ice melting [5] shows that significant overheating facilitates the formation of dendritic melt nuclei (Tyndall figures) with the largest surface areas. Then, with a decreasing degree of overheating and formation of new interfaces, the melt areas acquire equant shape and start to touch each other. The melt begins to float in the matrix along narrow channels, i.e., the system evolves with the separation of melting products from restite.

Melting of the crustal and mantle rocks presumably occurs in a similar manner. However, it is complicated by the polymineralic composition of rocks, when individual minerals vary in melting temperature, and their grains can be irregularly distributed over the rock volume. Melting is typically initiated at the contact of the least refractory minerals or along cracks in them. This is well seen in the lower-crustal xenoliths in the breccia pipe of Elovyi Island, Kola Peninsula (Fig. 1). Their melting was caused by heating of xenoliths in the host kimberlite-like magma and was stopped by quenching immediately after the explosion. Thus, the initial melting structures were conserved.

The initial multicomponent melt is lyophobic with respect to residual matrix minerals and is expelled from pores, capillaries, and fissures by the Laplace forces [2]. This was confirmed by experiments which showed that even an insignificant amount of the melt formed in peridotites under weakly dynamic conditions can migrate along grain boundaries from triple-grain spaces
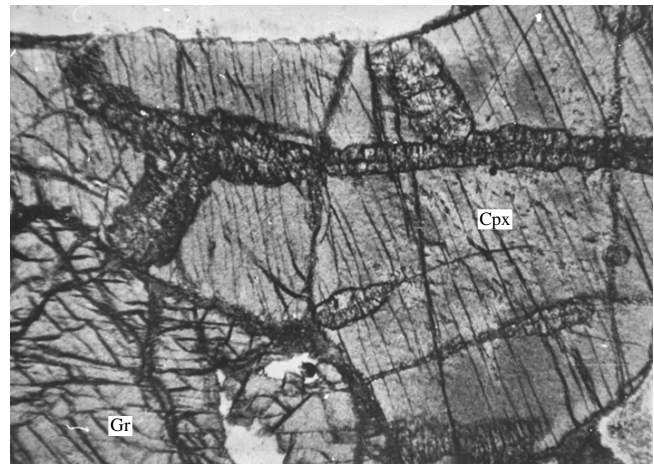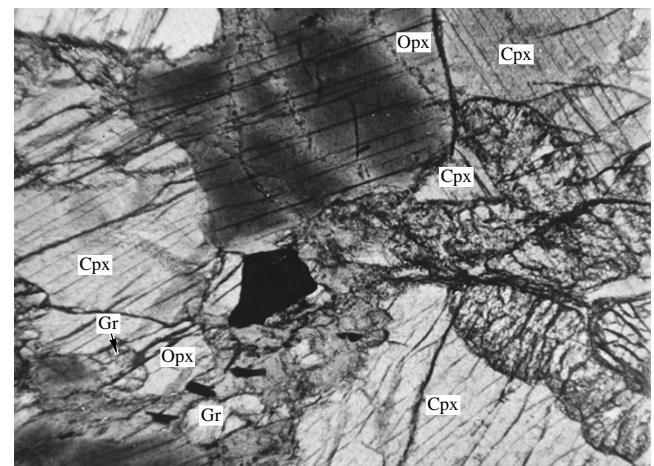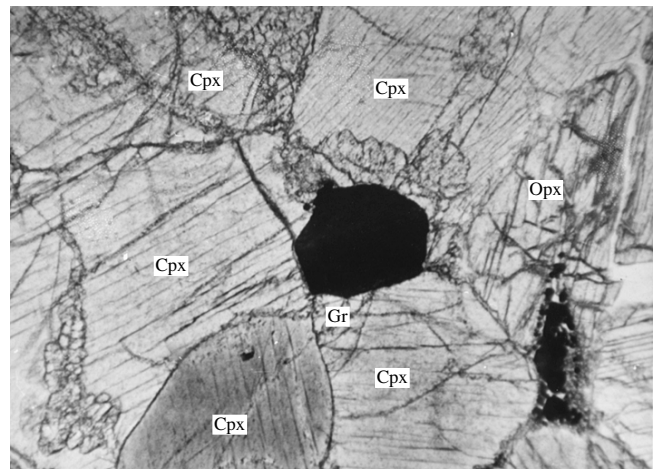

Fig. 1. Initial stages of melting. Xenoliths of the lower-crustal orthopyroxene-bearing granulitic eclogites from breccia pipe of Elovyi Island, Kola Peninsula. It is well seen that clinopyroxene melting (dendrites with irregular drop-like scalloped aggregates) began mainly along the fissures in minerals, as well as at the grain boundaries (black is rutile); orthopyroxene and garnet have not yet been involved in melting. Author's material. Microphotographs, Sample 27-14, magnification 50.
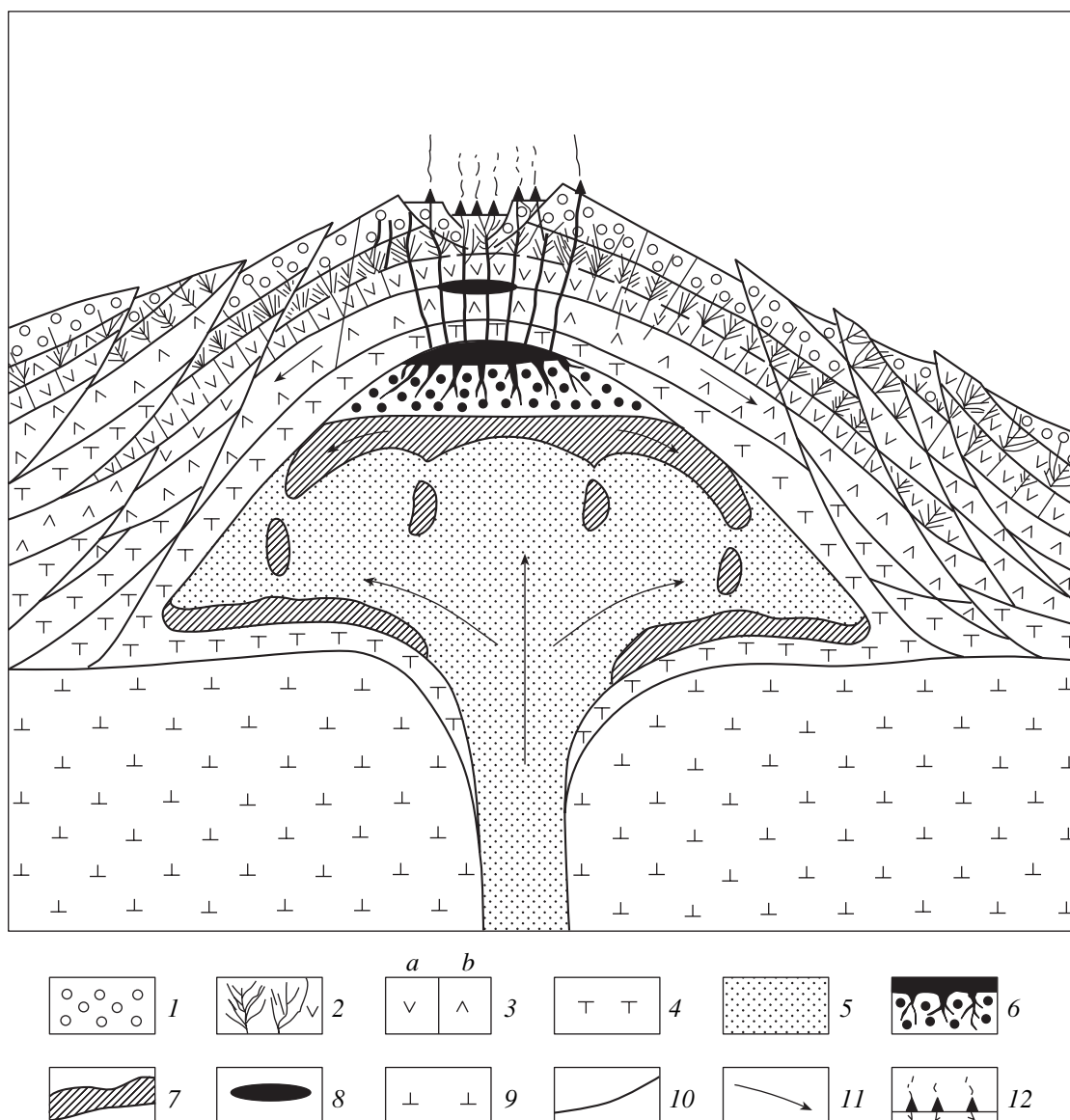
Fig. 2. Inferred structural scheme of a magmatic system beneath the axial part of a mid-ocean ridge. (*1*) Pillow lavas; (*2*) sheeted complex; (*3*) gabbroic complex (solidified products of the main lower crustal chamber, which accumulates mantle melts): (*a*) lower layered gabbros, (*b*) upper "isotropic" gabbros; (*4*) marginal cooled part of mantle plume from oceanic spreading zone; (*5*) asthenospheric material of the plume; (*6*) melting zone; (*7*) refractory residue; (*8*) magmatic chambers; (*9*) ancient oceanic lithosphere; (*10*) faults; (*11*) direction of motion of mantle material; (*12*) submarine volcanoes.

where it forms [6]. This possibly explains the nearly complete absence of notable amounts of newly formed melt in the mantle rocks: ultramafic (mantle) complexes of ophiolite associations and mantle xenoliths in basalts and kimberlites. At the earliest melting stages, the melt migration can be recognized only by geochemical methods [7–9].

Like in the case of ice melting, the melt should ascend in the matrix along narrow channels, which gradually widen upward owing to wall melting, i.e., the melting system is fractionated into melting products and restite. For instance, the restite origin can be inferred for dunite veins (extremely depleted mantle material), which are often observed in mantle ophiolite complexes [10]. During further ascent of newly formed melts, the pathways of their migration in relatively cool, upper parts of mantle plumes are typically well preserved as dike- and veinlike pyroxenite bodies [9].

It was shown earlier [2] that the melt extracted from crystalline rock tends to be accumulated along isobaric–isothermal surfaces, which presumably explains the migmatite banding in areas of crustal magma generation. Such structures are rare in the mantle rocks, and are mainly observed in tectonic blocks of mantle rocks in orogenic zones, such as Beni Bousera in Morocco, Ronda in Spain, and Horoman in Japan,

where mafic and ultramafic rocks form thin alternations resembling migmatite structures [10–13]. Such structures are believed to originate by partial melting of peridotites due to their ascent and decompression. Such structures are still rarer in mantle rocks of ophiolite associations [14, 15] and are almost completely absent in mantle xenoliths, which present fragments of the upper marginal parts of plumes, where no magma formation occurs [16].

Newly formed liquids are accumulated in large amounts to form magma chambers under the cool upper margins of plumes [2]. Such chambers are found by detailed geophysical studies beneath mid-oceanic ridge axis [17, 18] (Fig. 2). The thermal energy released on cooling of these chambers can be partially transformed into mechanical work, and the melts can be transported to shallower levels or to the surface. This is stimulated by magma buoyancy with respect to solid restite, by the effect of lithostatic pressure, as well as mechanical processes caused by gravitational instability above magma chambers, with submergence of roof blocks into the magma and the subsequent magma ascent.

Thus, melting under static conditions is a frontal process. Melting begins on adiabatic decompression due to the ascent of hot asthenospheric plume material to the depths where its temperature exceeds solidus. Newly formed melts migrate upward in intergranular spaces, gradually expand, and are accumulated as magma chambers beneath cool upper margins of plumes. Then, they can be transported to the surface through systems of intermediate crustal chambers. In the case of thin oceanic crust, the main chamber is located immediately on the cooled plume roof, where mantle-derived melts are accumulated [19].

Refractory restites should be accumulated in the lower parts of melting zones; they can be melted again only during further ascent of the magma generation area, further decompression, or invasion of new hotter material from the mantle depths. Melting in the sialic crust presumably takes place above intermediate chambers of basaltic magmas, which provide excess heat for the onset of melting.

Melting under Dynamic Conditions

Effects of the interface formation presumably play an especially important role in subduction zones, which generate calc-alkaline melts. Subduction zones are zones of extensive compression and originate by active interaction between lithospheric plates (1) at the active continent–ocean boundaries, for instance at the Pacific Ocean periphery, where an oceanic plate is subducted beneath a continent, and (2) in zones of continental collision, for instance, in the Alpine–Himalayan belt. The subduction zones are typically characterized by a compression regime. However, Sharapov *et al.* [20] analyzed the trajectory of the main strain tensors in the Kurile–Kamchatka arc for depths of 0–35, 40–120, and 120–130 km and showed that each interval contains extension areas at prevalent compression regimes. The mechanical state of subducted plates is generally unknown. Are they massive bodies or do they present thick sheared zones, along which cold material of the upper lithosphere slips in the middle and lower mantle? Available geological, petrological, and geomechanical data support the latter viewpoint [21, 22].

Melt generation in this setting strongly differs from melting on adiabatic decompression in the hot mantle plume heads or heated Earth's crust above them. Subducted plates are traced to depths of 650–800 km and remain brittle, i.e., they are seismically active throughout their entire extension. The presence of the Benioff seismic zone indicates that the plate material is not heated enough in contact with ambient hot mantle during descent. Otherwise, this would inevitably lead to a decrease of viscosity and loss of the ability to accumulate the tensions in the rock required for earthquakes. Existing attempts to explain magmatism by friction of the subducted plate roof with a mantle wedge cannot explain the phenomenon, since, according to seismic data, most earthquakes are restricted to the upper and lower boundaries of the plates. Moreover, these data suggest that melting zones are located inside the subducted plates [23].

Thus, the subducted plate remains relatively cold to depths of 600–800 km. At the same time, it locally experiences extensive melting episodes, after which it rapidly cools, continues moving downward, and retains rigidity, in spite of contact with ambient hot mantle. This indicates that the subducted plate is an autonomous self-regulating adiabatic system. Adiabatic behavior can be related to the following two factors: (1) relatively low thermal conductivity of rocks and (2) high rate of heat release, when no efficient heat exchange with the ambient medium is possible.

The processes related to the interface phenomena and described by thermodynamics of complex systems [2] are fairly efficient in this setting. These processes can be periodic and abrupt and can lead to accumulation and the rapid release of a large amount of energy required for magma generation.

The melting in the compression zones seems to be thermodynamically unfavorable, since the solidus temperature significantly increases with pressure increase. This is true for experimental systems (massive phases). Data available in reference books are also ascribed to the massive phases.

However, contrary to the concepts of many tectonists and geophysists, the subducted "plate" is not a plate as a mechanically homogeneous massive phase. Observations in the ancient subduction zones show that their rocks experienced extensive bulk shearing with formation of penetrated structures and granulation, i.e., comminution to tenths to hundredths of a millimeter. Since the dispersed matter possesses a higher surface energy than the massive phase, the transition of such
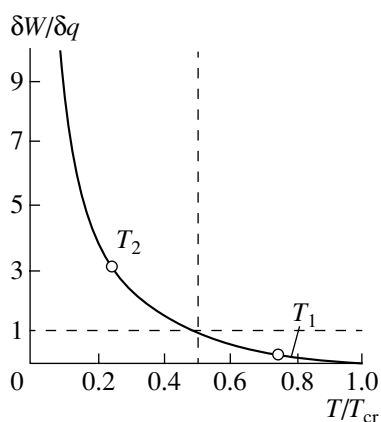
Fig. 3. Relations between supplied mechanical δW and thermal δq energies during isothermic formation of interphase in the heterogeneous thermodynamic system as a function of temperature. After Eroshenko and Sharkov [2]. T_{cr} is the critical liquid temperature, at which δ (surface tension) is equal to zero.

matter into the liquid phase requires significantly less heat energy. However, the role of high pressure, including non-hydrostatic one, in decrease of melting temperature consists in accumulation of excess elastic energy in rigid matrices [21].

Decrease of melting temperature of highly strained crystals in a massive phase can be explained in the following way. At high pressures and high mechanical strain, interatomic and intermolecular bonds, respectively, in crystals are ready to break. Hence, small fluctuations of temperature or pressure (strain) can cause abrupt and rapid break-up of these bonds in crystal lattices, which are in a "stress" state under high pressure. The avalanche break-up of crystalline matter into individual molecules and clusters (cybotaxes) ([3]) leads to highly efficient disintegration of the massive phase (decomposition to microdomains) with formation of a highly developed interface. As a result, solid and liquid clusters of different ordering degrees can coexist within a certain temperature interval [24]. All transformations in deformed crystal occur in its lattice, which is on the verge of destruction or already in the process. These phenomena decrease the melting temperatures of rocks [21, 25].

Decrease of solidus temperature is also related to high water contents typical of the subduction-related melting substrates [26]. Very fine-grained disintegration leads to homogenous penetration of aqueous fluid owing to capillary wetting forces; this also facilitates the accelerated melting. Given the aforesaid effect of lower melting temperature of the disintegrated phase compared to that of the massive one, the magma formation in subduction zones can be explained by a decrease of melting temperatures of the rocks rather than an increase of environmental temperature. The volume increase on melting (melt is 11–13% larger in volume than the primary solid rock) should cause the formation of new fissure networks (i.e., additional brecciation of

solid phase), an increase of its bulk surface area, and acceleration of melting. Thus, the considered mechanism implies that zones of intense compression present the areas of accelerated melting.

The heat source is the most important problem for understanding magma formation within subduction zones. As mentioned above, the large-scale interface development is an endothermic process, i.e., it requires a heat supply. This follows from the equations [21]:

$$q_\Omega = Td\delta/dT\cos\theta\Delta\Omega,$$

$$dq_\Omega/dt = Td\delta/dT\cos\theta d\Delta\Omega/dt,$$

where $\Delta\Omega$ is interface increase (in m^2), t is time (in seconds), T is temperature (°C), δ is surface tension, q_Ω is energy of interface formation, θ is contact angle.

In the case considered, the heat consumption is high enough to compensate for the heat emission of internal friction (ductile dissipation) and to significantly neutralize heat contact with the ambient hot mantle. In spite of limited thermal conductivity under rapid plate subduction (4–10 cm/y [4, 20, 27]), this process presumably plays an important role in the formation of thermal troughs in the subduction zone and preservation of the plate quality to remain brittle over its entire extension.

On the other hand, expansion in the dispersed systems in the absence of efficient heat exchange with the environment, i.e., in adiabatic systems, is accompanied by rapid temperature increase at the expense of accumulated surface energy released on interface reduction. As was shown earlier [2], heat and work of formation of an interface unit in an isothermal process are related by a certain equation (Fig. 3), where δW is supplied mechanical energy, δq is supplied heat, and T is temperature of the process. It is seen from Fig. 3 that at $\delta W/\delta q > 1$ (field of relatively low temperatures and high pressures) mainly mechanical energy is accumulated (or released), whereas, at $\delta W/\delta q < 1$, heat energy is accumulated (or released). In other words, when the primarily cold and strained material of the subducted plate enters the zone of relative decompression, the interface area is rapidly reduced, and the rock temperature consequently increases.

As mentioned above, compression and extension domains alternate in a subducted plate along its dip. Entering such discharge zones, the subducted material should be heated to solidus (and higher) temperatures at the expence of accumulated energy. This is a large-scale process, which can involve significant volumes of subducted material melting.

All thermomechanical processes in the magma generation zone, which finally lead to temperature increase (friction, heat supply from host mantle rocks, and interface reduction), facilitate the magma formation. Heat released on interface reduction presumably serves as a trigger for abrupt and rapid magma formation, since friction and heat supply from ambient mantle only compensate for the decrease of plate temperature during endothermic interface development. Increase of

melting productivity is facilitated by the aforesaid decrease of melting temperature in the dispersed, preliminarily strained environments, as well as the universal presence of aqueous fluids. According to seismic data, the magma generation areas beneath island arcs are mainly formed at depths of 120–130 km [28], which coincide with one of the zones of relative extension [20] and are consistent with the proposed model.

The second paradox of magma formation in the subduction zones is that rheological and thermodynamic properties of the environment abruptly change with melt appearance mainly at the expense of a strong decrease of internal friction and extent of the environment disintegration, owing to predominant melting of brecciated areas and a total decrease of the interface area. This sharply decreases the generation of friction heat, particularly when some part of the heat is absorbed by the melt having high heat capacity. All this leads to the rapid cooling of the melting zone and cessation of magma formation. Cooling causes the expulsion of the melt from pores and capillaries of the host rocks [2, 21]. This process occurs intermittently. Newly formed melt should be rapidly removed from the magma generation zone. Otherwise, the melt would be solidified and not reach the surface, in spite of the large amount produced by accelerated melting.

Numerous attempts to explain the removal of newly formed melt from magma generation zones by exclusively mechanical processes, in particular, by filter-pressing, failed, since such mechanisms can only partially remove the melt, whereas some part of the melt remains in interstices between solid fragments in the melting zone. Therefore, we believe that further extraction of the melt after its partial mechanical removal is related to lyophobic behavoir of the melt with respect to matrix. As was shown above, during cooling of such a heterogeneous system, internal pressure of the liquid phase, determined by the Laplace capillary pressure, increases owing to an increase of the surface tension of the melt. This causes spontaneous extrusion of liquid magma from pores and capillaries with the formation of large magma chambers (Fig. 4). Evidently, such chambers should be located beyond the subduction zone, within mantle wedges, which, as was established by seismic tomography in some island arcs, produces melts for island-arc volcanoes [29–31]. The inferred scheme of this process is shown in Fig. 5.

The subducted plate moves further downward. The $\delta W/\delta q$ ratio again becomes larger than one, i.e., the process is again accompanied by energy (heat) consumption at the expense of development of translation interfaces. Again, the matter is disintegrated, cools, and becomes brittle and seismically active. Then, the melting can proceed when the plate enters the extensional conditions. Available data indicate that magma formation in subduction zones mainly occurs within the depth range of 100–200 km [4, 28, 30]. It is possible that at shallower depths, pressure was too low to produce a
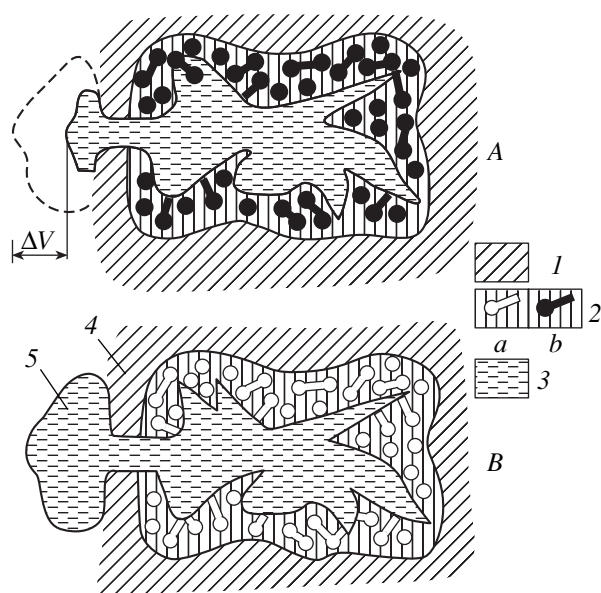

Fig. 4. Scheme of physical interaction of the melt with host rocks for incompressible framework of the intrusion. (*A*) Melting area with a magma chamber, (*B*) system after beginning of cooling. (*1*) Undeformed rocks; (*2*) outer-contact fissured and porous rocks (*a*) with unfilled pores and (*b*) with filled pores and fissures; (*3*) melt. Numbers in the figure: (*4*) feeder, (*5*) extruded volume of the melt (newly formed magma chamber).

sufficiently strained state, while at greater depths the solidus temperature increases so high that heat generation becomes insufficient for melting.

Thus, the presented model suggests a mechanism of intermittent magma formation in subduction zones. It is highly improbable that the subducted plate was burned through over its whole extent during magma formation. The local occurrence of melting zones such as molten pockets is more possible, which can be indicated by chains of volcanic centers in island arcs and active continental margins. Unlike the subduction-related melting zones, which are rapidly initiated and disappear, magmatic chambers in the mantle wedge operate for a long time, thus maintaining the activity of large magmatic centers beneath island arcs, active continental margins, and volcanic arcs in the collision zones. Since melting zones in the subducted plate are located in areas with optimal physical parameters, new melting zones will be rejuvenated there owing to the supply of fresh subducted material. Evidently, new melt will feed magma chambers in the mantle wedge, thus providing their continuous existence.

Such chambers accumulate much heat energy, which is transformed into mechanical work during magma eruptions. However, unlike the areas of oceanic spreading and intraplate magmatism, magma chambers in the subduction zones are located at larger depths. The chambers move stepwise to the surface. Since their displacement and occupation of new volume are highly
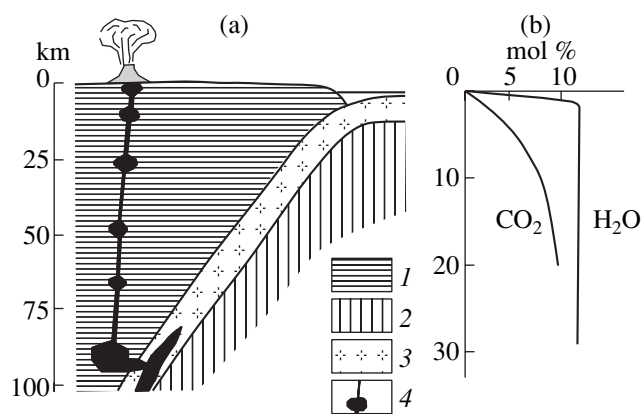
Fig. 5. Scheme illustrating the structure of the magmatic systems related to subduction zones at the active margins of continents and oceans. (a) Structure of the system: (*1*) continental lithosphere, (*2*) oceanic lithosphere, (*3*) subducted plate, (*4*) magma chamber. (b) Variations of H_2O and CO_2 solubility in silicate melt versus pressure (simplified after [32]).

energetic processes, the formation of a new magma chamber at a higher level should be accompanied by wide development of brecciation zones and respective increase of interface area. The process efficiently repeats until magma reaches the shallow chamber or surface [2]. In other words, the melt stepwise migrates upward in such conditions (Fig. 5).

ROLE OF INTERFACE FORMATION DURING RETROGRADE BOILING OF MELT ON DECOMPRESSION

Boiling of melt is one of the most important magmatic processes, which often leads to significant geological consequences, in particular, to catastrophic volcanic eruptions. The physical essence of this phenomenon is as follows: the decrease of temperature and pressure causes the decrease of gas solubility in the melt. If the melt is saturated in volatiles, it can spontaneously expel the gas, i.e., begins to boil [4, 32–34]. The scale of this process evidently depends on initial fluid saturation in the melt and its energy state related to the formation and growth of gas bubbles in the melt. Since magmas, especially basaltic melts, have a rather low fluid content, retrograde boiling on decompression plays only a subordinate role. However, the situation sharply changes in the subduction zones, where magmas are saturated in water, and the scale of magma boiling and its consequences are significant.

Retrograde Boiling Related to Degassing of Intraplate Basalts

Cenozoic intraplate basaltic volcanic products are widespread in continents and oceans and, therefore, are well studied. The volcanic occurrences are related to the activity of mantle plumes, the heads of which rapidly spread at shallow depths, forming continental rift areas, flood basalt provinces, and oceanic island-type volcanic centers. Intraplate basalts normally compose large shield volcanoes or giant lava plateaus formed by fissure eruptions. Central-type volcanoes are rare. Instead, we observe chains of cinder cones, which originated at the final stages of lava plateau evolution and trace feeder channels. Lavas are mainly represented by massive varieties; gas cavities in rarer vesicular lava flows are confined to their upper parts, where the rocks can grade into scoria. Basaltic lavas often contain specific subvertical, irregular, often branching pipelike cavities and porous cylinders ("gas pipes") from a few to 10–15 cm across [35]. The formation of cinder volcanoes is often accompanied by explosions with the formation of pyroclastic cones no more than a few hundred meters across and 100–200 m high. Cinder and pyroclastic cones often contain numerous mantle xenoliths (probably from the cooled upper part of the plume above the melting zone) [16].

The study of the fluid phase of intraplate basalts showed that gases mainly consist of CO_2 and less abundant H_2O; significant amounts of Cl and F also occur [26, 36].

The presence of vesicular varieties, together with massive lavas, evidently indicates that magmas were solidified under conditions close to fluid saturation. When fluid solubility decreases with decreasing temperature of the melt, the gas phase begins to release spontaneously; degassing occurs together with crystallization, thus indicating retrograde boiling. This is supported by the facts that acicular plagioclase and pyroxene crystals pierce vesicle boundaries, and vesicular rocks are confined to the upper parts of lava flows.

It is interesting that vesicular lavas are normally more glassy than the massive lavas. Scoria and "gas pipes" are most glassy rocks and mainly consist of volcanic glass with small amount of crystals and crystallites. All these facts indicate a positive correlation between glass content and abundance of gas bubbles in basalts. If this was related to the better preservation of gas bubbles in glassy lavas, the rock would remain glassy at a distance from cavities. This is presumably related to the fact that the formation of the liquid–gas interface requires more energy than the formation of liquid–solid (crystal) interface.

The vesicular "gas pipes" are higher in Ti, Fe, alkalis, P, Ba, and other incompatible elements than host basalts [35]. Similarly, the material of cinder–pyroclastic cones and tuffs are also enriched in these components relative to lavas [37]. These components are typically the main constituents of mantle fluids, which provide mantle metasomatism and participate in generation of intraplate mantle melts [10]. These fluids are presumably liberated as a gas phase during melt cooling.

As mentioned above, the cinder–pyroclastic cones form at the final stages of lava plateau evolution. The

matter of these cones represent the last portions of the melt during the final emptying of the mantle magma chambers, which are located in the upper parts of local uplifts in the plume roof. This melt should be significantly more saturated in fluid than lavas of previous eruptions. This could be related to gradual exhaustion of the mantle magma chambers, and more rapid supply of the deep–seated fluid than of the newly formed melt. The last portions of the melt were most saturated in fluid. Retrograde boiling in them presumably began during ascent under shallow conditions, when the limit of gas solubility and the energy barrier of the bubble nucleation were exceeded.

Under such conditions, the further events may follow two naturally occurring scenarios: (1) expulsion of the melt as foam with formation of cinder cones and (2) explosive eruption with formation of volcanic ash and pyroclastic cones. In the first case, the large-scale spontaneous formation and growth of bubble nuclei leads to the rapid heat removal and melt vitrification. Its viscosity rapidly increases, the flow character rapidly changes, and lava is squeezed out as thick foam. The bubble nucleus formation follows isotherms and generally has a frontal character. The scale of bubble formation is insignificant at each moment, and the eruption is relatively quiet. Equant shape of vesicles indicates that the foam is "wet," i.e., contains large melt proportion [38]. This, in turn, indicates a rapid supply of newly formed foam at the surface, since otherwise, the wet foam would be rapidly transformed into "dry" pumice-type foam owing to drainage of the melt between bubbles (or bubble floating). Explosions that occasionally associate with cone formation are presumably related to the presence of some water amount in the melts. This problem will be considered in detail in the next section.

Of special interest are kimberlite breccia pipes, which contain xenoliths, including diamond-bearing ones, and which sample the deepest portions of the lithosphere. As was shown by experiments [39], the CO_2 solubility in the kimberlilte melt depends on the Ca/Mg ratio and sharply decreases within the pressure range from 40 to 50 kbar. This should cause an abrupt release of gas from arising fluid-saturated kimberlite or lamproite melts and should lead to explosion. The depth of the explosion depends on the above ratio and ranges from 140 to 170 km, i.e., spans the depth of diamond occurrence. The power of the explosion was high enough to transport xenoliths of the mantle material from these depths to the surface.

Boiling of the Subduction-related Melts on Decompression

As mentioned above, these melts mainly belong to the calc-alkaline series, which is typical of zones of active interaction of lithospheric plates. As compared to intraplate basalts, retrograde boiling is widely abundant in calc-alkaline melts and often leads to catastrophic volcanic explosions (Fig. 6). These explosions are
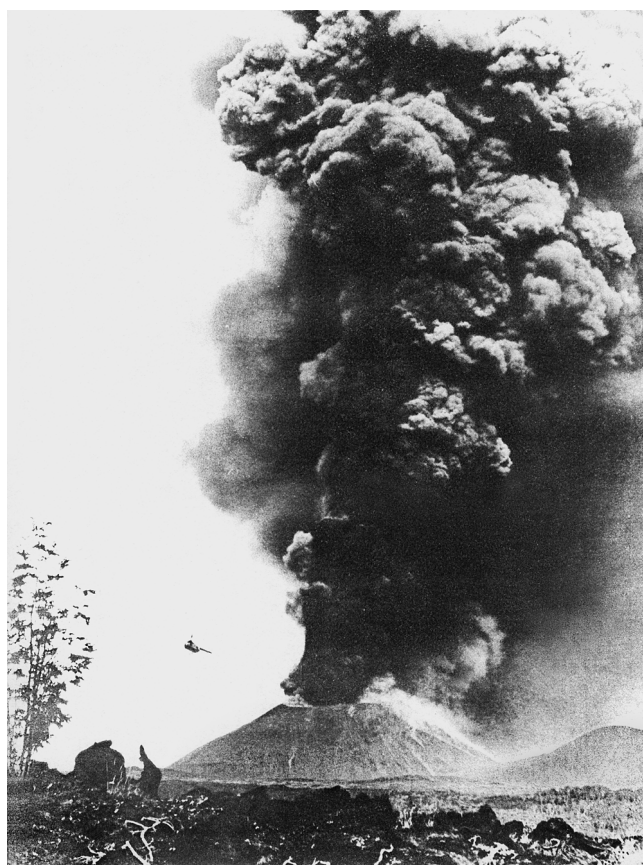

Fig. 6. Explosion of Tolbachik volcano, Eastern Kamchatka. Photo by A.P. Khrenov.

accompanied by the ejection of vast amounts of gases and pyroclastic material, glowing clouds, surges etc.; lead to great human and material losses, as well as exerting a significant, in some cases, long-term impact on the Earth's atmosphere and climate.

Let us consider several examples. The relatively small explosion of the St. Helens volcano in the northwestern USA in 1980 swept an area of 29 km in radius around the volcano, caused ash falls, landslides, mudflows, and floodings; explosions lasted two months [40]. During the explosion of the Krakatoa volcano (Indonesian arc) in 1883, 20 km^3 of pumice and ash were ejected into the atmosphere [41]. The large-scale explosion of the Tambora volcano in the same arc in 1815 produced 150–180 km^3 of pyroclastic material [41]. Explosions of these volcanoes, owing to the ejection of large amounts of dust and gas, significantly decreased (by 0.5–0.8°C) the average Earth's temperature for 1–1.5 years. The study of the El Chichon volcano in Mexico in 1982 [42] showed that its products contain a large amount of sulfur, which was oxidized to sulfuric acid to form long-lived fog. Such aerosols also screen solar radiation, thus decreasing the average temperature by 0.2°C. The amount of sulfuric acid aerosol in this case was estimated as 20 million tons. Explosion

of the Pinatubo volcano (Philippines) on May 14–15, 1991 produced about 7 km^3 of rhyolite–dacite pyroclastics and 19 million tons of SO_3 [43].

Thus, these volcanoes (typically confined to the active plate boundaries) significantly affect atmospheric processes and are highly hazardous for humans. Therefore, the study of mechanisms of catastrophic explosions is one of the most important petrological problems. Both the catastrophic scale and long duration (2–4 months) of the explosions require explanation.

Most geologists suggest that catastrophic explosions are related to an abrupt increase of magma volume in shallow chambers owing to degassing. The relevant genetic models suggest the following causes of explosions: groundwater penetration into magma chamber [44], collapse of volcanic cone [41], emplacement of gas-saturated basaltic magma into dacite magma chamber [42], penetration of magma chamber by fractures–conduits [45]. Unfortunately, none of these models explains the vast scale and long duration of the process, as well as considering specific mechanism of the large-scale bubble formation required for such explosions. The above phenomena actually can affect the eruption style in some cases; however, they cannot cause the catastrophic scale. The hypothesis assuming gradual accumulation of volatiles near the roof of the magma chamber due to their ascent from deeper levels or due to directed solidification of the magma chamber also fails to explain catastrophic volcanic explosions [46, 47]. In this case, a gradual growth of gas bubbles should lead to the appearance of fissures in the roof, through which the gas will escape and excess pressure will be eliminated without explosion. However, this mechanism can explain catastrophic eruptions accompanied by the formation of glowing clouds (for example, the eruption which destroyed the town of Saint Pierre on Martinique island in 1902 [46]).

One more model assumes that the stationary ejection of the gas–pyroclastic material can be changed to an unstable state, when the process scale can increase by 2–3 orders of magnitude [33]. The main parameters controlling the eruption style in this case are the chamber depth, channel diameter, and magma viscosity. The "splitting" parameter that determines the bifurcation point is the chamber depth. The jump is possible if this depth is somewhat lower than some critical depth, which depends on magma properties. The duration of eruption is considered to be related to periodical plugging of the channel by material from its walls. The cessation of eruption is explained by the pressure decrease in the chamber. However, this model does not take into account the formation of gas bubbles as well.

All these hypotheses consider the explosion itself, but do not explain the high gas content in melts and the mechanism of practically simultaneous separation of gas bubbles in a significant volume. We believe that the process is mainly controlled by kinetic factors, because the formation of a new interface requires significant energy consumption [1, 2]. This is typical of any phase transition, including retrograde boiling of melt, which is considered here. Therefore, the formation of numerous nuclei of a new phase (crystals, melt, or gas) in the previously homogeneous medium can occur only after an energy barrier is overcome. Then, the process proceeds in large volume, since it operates within the stability field of the new phase. The formation of a few nuclei owing to fluctuations cannot be developed to a large-scale process, because the increase of an existing interface is energetically more favorable than the formation of a new one. Therefore, local decompression, for example, because of a fracture in the chamber roof, can cause the growth of one gas bubble or group of bubbles or lead to local magma foaming during filling of this fracture. However, it is unreasonable to expect the large-scale degassing, since conditions have not changed in the remaining magma volume. Evidently, the kinetic factor (rate of gas nucleus formation) constrains the evolution of volcanic eruption by the model proposed by Yu.B. Slezin [33], since new nuclei have no time to form in the catastrophic phase of eruption and the process becomes abruptly weaker.

Thus, the presence of volatile-rich magma as well as some energy pulse behaving as a "trigger," which causes the rapid and extensive formation of gas phase nuclei, is necessary for a long-term catastrophic explosion.

As mentioned above, most of the catastrophic volcanic explosions associate with subduction-related calc-alkaline and shoshonite–latite magmas containing water as the dominant volatile component [26]. Some water was introduced in the melting zone with the subducted plate, while some water could be extracted by these magmas from host rocks during their stepwise ascent with formation of intermediate chambers [48, 49] (Fig. 5). Owing to the high solubility of volatiles in magmas, especially in those of acid and intermediate composition, at high P–T parameters [32], the volatiles should be "sucked out" of host rocks of intermediate chambers.

According to experimental data [32], the solubility of water and CO_2 in mafic and felsic melts increases with pressure up to 30 kbar without extremes (Fig. 5). Unlike water, CO_2 solubility significantly depends on the melt composition, being the lowest in the felsic and intermediate magmas, whose eruptions are typically catastrophic. In other words, water should be the dominant component of the gas phase in rhyolites and dacites, as is the case in nature. The experimental data also indicate that water solubility in the melts remains nearly constant during pressure decrease to about 1 kbar and then abruptly decreases. Unlike water, the CO_2 solubility gradually decreases with decreasing pressure, and only weakly depends on the initial $CO_2/(CO_2 + H_2O)$ ratio.

This indicates that an andesite–dacite melt ascending from the magma generation area should intensely absorb water from host rocks. As a result, the melt

under shallow conditions in peripheral chambers of volcanoes at depths of 3–4 km can become oversaturated in H_2O owing to abrupt pressure decrease. In this case, melt in the magma chamber presents a blasting mixture, which is ready to explode at any moment owing to rapid degassing. Seismic observations show that the upper magma chambers in most andesite–dacite volcanoes are located at these depths (2–8 km) [33, 46, 47]. Hence, such phenomena frequently occur in nature.

However, as follows from experimental data, even the water-oversaturated melt cannot boil spontaneously without any additional impact or can boil only by foam formation, as takes place during the eruption of intraplate basalts (see above). Large-volume separation of gas bubbles requires a mechanical shock-type impact: the melt must be abruptly compressed and subsequently decompressed [34, 50]. In this case, gas bubbles begin to form over the entire magma volume. We believe that this mechanism can be applied to catastrophic volcanic eruptions. The volatile-saturated melt in a shallow chamber can explode owing to a strong earthquake, when pressure abruptly increases in the compression front and abruptly decreases in the subsequent expansion front.

This mechanism is especially efficient during a series of earthquakes, which usually precede catastrophic explosions, since the seismic events homogenize the melt and prepare it for retrograde boiling, which begins at the moment when the energy barrier is overcome. During a further (stronger) impact, many homogeneously scattered gas bubbles are formed in magma. It is highly improbable that the entire chamber volume is spanned by this process, since pressure in the chamber can increase downward to 1.5–3 kbar [46, 47], thus blocking further formation of bubbles. However, this pressure is sufficient for explosion and ejection of the material. At the moment of explosion, the magma chamber is impacted by the explosion-related shock wave, which is followed by the expansion front, thus again allowing large-volume degassing and a new explosion, and so on.

Such a mechanism determines the layer shape of the retrograde boiling zone related to frontal propagation of shock waves. The boiling layer may have any spatial orientation depending on shock wave direction, thus the ejections could be oblique [46, 47]. However, in any case, this zone, owing to explosions, will migrate downward, primarily develop in the shallower sections of the magma chamber, and gradually remove the melt from it. If the chamber has a significant vertical extent, it can be emptied to depths of about 5–6 km, since the melt at larger depths may be undersaturated in H_2O and retrograde boiling will stop. Calderas can form owing to the chamber emptying, and the volcano will become inactive until the formation of a new chamber by water-saturated magma replenishment, after which the process can repeat. However, this typically does not occur,

since subsequent magma portions supplied from magma generation zones have a lower water content because the lithospheric rocks along the magma conduits have already been dehydrated by previous magma portions. Therefore, a new Vesuvius-type cone can form in the caldera [46].

It is interesting that the volume of pumice and ash erupted during caldera formation as recalculated to the volume of nonporous magma is almost universally smaller than the caldera volume [46]. For example, the volume of volcanic ejecta related to the Shikotsu caldera on Hokkaido, Japan was about 50 km^3, while the volume of the caldera is 79 km^3. This can be related to the gradual expansion of the magma chamber during explosions, since internal pressure was maintained at a high level at that time. This may indicate that a part of the magmatic foam remained in the chamber, thus maintaining pressure in it, and this foam, unlike the melt, is compressible. Therefore, progressively larger volume of the remaining material should be involved in the explosion. This is consistent with the fact that the strongest explosions typically occur in the end of eruptive cycle [46, 47].

Thus, the most important prerequisites for the catastrophic explosive volcanic eruption are as follows: (1) presence of water-saturated felsic–intermediate melts in shallow chambers at depths of 3–5 km and (2) seismic activity of the region. The presence of other volatiles (CO_2, SO_3, etc.) plays no significant role. This could explain the relative scarcity and small scale of explosive processes during intraplate magmatism, which is dominated by eruptions of moderately alkaline basalts with CO_2 as the main volatile. However, this does not exclude strong explosions in the shallow trachyte and trachyrhyolite chambers, which occasionally occur in such regions.

CONCLUSIONS

(1) The energy of interface formation is an important parameter that controls the evolution of magmatic systems. The energy factor plays a critical role during phase transition at the beginning of crystallization, melting, and retrograde boiling, when numerous nuclei of one phase are formed within another phase. The beginning of phase transition requires an additional energy contribution (a special trigger of the process), which is spent in the interface formation.

(2) The interface formation also plays an important role in the macro-scale processes, i.e., during the formation of melting zones and during retrograde boiling of melts. The latter leads, in some cases, to catastrophic volcanic eruptions.

(3) The melting style significantly depends on geodynamics. Under "static" conditions (oceanic spreading or intraplate activity), the magma generation mainly occurs by melting zone propagation due to decompression in the upwelling plume. Newly formed

melts travel upward along the system of intergranular spaces and are accumulated beneath the upper, cooler zone of the plume to form the magma chamber. Under dynamic conditions (subduction zones), the bulk periodic melting is observed.

(4) Unlike melting, the retrograde boiling strongly depends on the composition of volatiles dissolved in the melt. Depending on this, the boiling can develop in layers or in the bulk volume. When CO_2 is the predominant fluid component, the boiling normally develops in layers. This leads to the formation of foam, which is extruded from the shallow magma chambers as cinder cones at final stages of the basaltic lava plateau formation; occasionally, this process is accompanied by insignificant explosions, which generate cinder–pyroclastic and pyroclastic cones. These magma chambers could be located in the upper parts of local rises in the plume roofs, which is evidenced from the frequent occurrence of mantle xenoliths in pyroclastics of these cones.

(5) Explosive eruptions are typical of the deep-seated kimberlite and lamproite magmas. In this case, the explosions could be related to the abrupt decrease of CO_2 solubility in the ascending fluid-saturated melt at 40–50 kbar. The power of the explosions was high enough to transport xenoliths of the mantle material from depths of 140–150 km to the surface.

(6) Bulk boiling of the water-saturated melts, which is often accompanied by catastrophic explosions, is typical of the shallow magma chambers. It is presumably related to the abrupt decrease in H_2O solubility at $1-1.5$ kbar in the subduction-related acid–intermediate melts. The presence of other volatile components (CO_2, SO_3, and others) exerts no significant effect. This is consistent with the relative scarcity and significantly lower scale of explosive processes during intraplate magmatism, which mainly generates moderately alkaline basalts containing CO_2 as the main volatile.

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