

Behavior of Kimberlitic Garnets Exposed to Chemical Weathering in Laterite Profiles: An Experimental Study and Stability Implications (Experimental Studies of the Kimberlitic Garnets Behavior at Conditions of the Laterite Chemical Weathering)

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ABSTRACT

The behavior of kimberlitic garnets involved in chemical weathering in lateritic provinces were studied experimentally using garnets of different paragenetic groups. In natural lateritic environments, garnets experience dissolution showing similar patterns worldwide. The tests were performed with the etching agents of hydrofluoric acid (HF), which never occurs in the free form in nature, and ATP-Na₂, an organic solvent common to biological systems and soils; the two etchants produce the same effects on grain surfaces. The dissolution rate (chemical stability) of garnets depends on CaO and Cr₂O₃ contents: Cr₂O₃ controls more strongly the behavior of peridotitic high-Cr garnets (from lherzolite and harzburgite-dunite) while CaO is the main stability control in eclogitic garnets with Cr₂O₃ < 0.5 wt. %. Unit cell size is another characteristic control of chemical stability of garnets. Garnets with bigger unit cell parameters tolerate better chemical weathering but the stability decreases in the garnet series from harzburgite-dunite to eclogite parageneses. The weathering stability difference among the garnet varieties leads to changes in initial proportions of kimberlite mineral assemblages during the weathering processes: low-Cr garnets disappear rapidly while the percentages of diamond-related garnets increase. The applied experimental conditions faithfully reproduce natural processes and provide explanation to effects observed in the field. The reported results have important implications for diamond exploration.

KEYWORDS

Garnet, Lateritic Weathering Crust, Etching, Paragenesis, Unit Cell Parameter.

Introduction

Kimberlite indicator minerals (KIMs) that originated in the Earth lithospheric mantle at high pressures and temperatures are unstable when become exposed to the Earth surface conditions and experience various changes, including physicochemical alteration. The conditions of laterite

weathering profiles (LWP) are especially aggressive toward the KIMs (Afanasiev et al., 2001). Minerals from Middle Paleozoic kimberlites in the Siberian craton bear signatures of dissolution in Late Devonian laterite profiles (Afanasiev et al., 2013a); laterites of different ages left imprint on KIMs from Precambrian formations in diamond provinces worldwide. The same KIM features are known for modern weathering profiles of Africa and South America.

Data on chemical (lateritic) weathering of KIMs (especially garnets) from the Siberian craton are highly informative. Signatures of such weathering in minerals provide solid evidence of their origin from Middle Paleozoic kimberlites, because lateritic weathering of Siberian kimberlites with significant dissolution of their minerals was during just a single event in the Late Devonian, while later weathering was not lateritic and did not cause such a strong effects on minerals (Afanasiev et al., 2013a). This fact has important implications for exploration of Middle Paleozoic diamond-bearing kimberlites in the Siberian craton. Furthermore, the degree and extent of chemical weathering recorded in the KIMs of Siberia agree well with the path of its motion in the Phanerozoic. In the Late Devonian, during the first known for Siberian craton event of Phanerozoic kimberlite magmatism, Siberia was located near the equator in the Northern Hemisphere, in climate conditions favorable for lateritic weathering, especially in its southern part (Cocks and Torsvik, 2007). Since that time, the continent moved northward and reached its present position in the latest Mesozoic, with its former southern part in the north, because the block was rotating slowly while moving. As a result, lateritic weathering of KIM assemblages in Middle Paleozoic kimberlites is the strongest in Arctic placers but is moderate in the Irkutsk and southern Krasnoyarsk regions (Afanasiev et al., 2013a). Thus, studies of samples from the Arctic areas of Siberian craton appear to be the most promising in this respect.

Chemical weathering in laterite profiles impacts crystal morphology, as well as the composition of KIM assemblages consisting of minerals that differ in physical and chemical stability. Investigation into the behavior of minerals exposed to weathering is of special practical interest. However, the nature offers only the final products for research while reconstructing the processes requires experimental studies. In our earlier experiments of etching in hydrofluoric acid (HF), the authors of the present research observed dissolution patterns similar to those in natural samples (Afanasiev et al., 2001). However, HF never occurs in the free form in nature, and it is important to try organic solvents which are common to natural biological systems and soils and thus better reproduce natural reactions.

Chemistry-controlled difference of garnets (pyropes) of variable composition in terms of stability to chemical weathering in laterite profiles leads to changes in mineral assemblages of KIM dispersion trains (Afanasiev et al., 1984, 2001, 2010). Garnet is a main kimberlite indicator mineral and the principal guide to its primary kimberlite sources (Sobolev et al., 1973; Pokhilenko et al., 1993; Pokhilenko and Sobolev, 1995, Dasgupta et al., 2009, Sun, Liang, 2014). Theoretical and experimental studies of weathering effects in garnets can resolve the problem of identifying KIM trains, which is hard to do from garnet compositions only because weathering biases the original relative percentages of different garnet varieties and erases the features of primary crystal morphology and mechanic wear that preceded dissolution.

Main objectives of the reported experiments were to reproduce surface features of garnet grains similar to those resulting from natural dissolution, to estimate dissolution rates in garnets of different paragenetic groups and compositions, and to distinguish the dissolution controls.

Choice of Suitable Etchants

In the 1970s the authors (Afanasiev et al., 1984, 2010) performed laboratory etching experiments on garnet, using inorganic acids (and their mixtures) and alkalis as etchants, in order to obtain surface patterns resembling those observed in minerals from natural laterite profiles. Hydrofluoric acid was the only reagent able to dissolve garnets for a reasonable period of time (visible etch microtopography appeared in three to five days) and produced surface patterns very similar to those in nature. Other acids and alkalis caused no marked effect, except for very subtle microtopography in orange garnets etched for 18 months in H_2SO_4 , which however left intact violet garnets (Afanasiev et al., 2010).

H. Carstens (1969) applied etching with hydrofluoric acid (HF) to bring out structure defects in garnets from Norwegian peridotites and obtained dislocation structures similar to those in naturally occurring weathered garnets. Similar results were reported by C.P. Gravenor and R.K. Leavitt (1981) who leached crushed garnets in various strengths of acid (HF) and alkaline (NaOH) solutions. Detrital garnets etched in HF developed patterns on the surfaces similar to the natural structures but were stable to alkalis.

The authors (Afanasiev et al., 1984) also carried out experiments to estimate relative chemical stability of different color groups of garnets (orange, red, violet, and green) to dissolution in HF. After 45 days of continuous exposure to HF, violet garnets lost 28% of their initial weight, while the red and orange varieties lost, respectively, 70% and 93% on average; green garnets with high content of uvarovite component showed no weight loss after more than a month of etching. Thus, the authors concluded that dissolution rates in garnets have a positive relationship with their Cr enrichment.

There are other agents besides chemical weathering that can affect mineral surfaces in a similar way, such as diagenetic dissolution, postmagmatic resorption along the margins of differentiated trapp sills, or orogeny-related processes (Afanasiev et al., 2001, 2010). However, the garnets altered by diagenesis, magmatic, or orogenic effects are morphologically different from those from lateritic conditions, which makes crystal morphology a proxy of tectonic settings. The fact that etching in HF, which never occurs in nature in the free form, faithfully reproduces natural dissolution patterns means that it acts, in a sense, in the same way as natural solvents, mainly organic and carboxylic acids. The reason is that like organic acids, HF is an active complex-forming agent and acts selectively on minerals: it dissolves some components and makes others insoluble. Namely, SiO_2 is leached from silicates with formation of dissolved solids, ferric fluoride is likewise soluble, while Mg, Al, and Ca fluorides remain on mineral surfaces and inhibit further reactions.

Proceeding from the similarity principle, which is often successfully used in experiments, the similarity of surface structures in laboratory HF-etched garnets with their natural counterparts makes us expect the same similarity in the chemical behavior. The authors of the present research

are aware that the laboratory modeling conditions are only some approximation of the long-lasting geological processes.

Thus, the authors infer that hydrofluoric acid can be used for modeling the processes and effects produced by lateritic weathering on garnet grains surfaces, as well as for estimating dissolution rates in garnets of different compositions. These estimates can be extrapolated to natural processes and employed for interpreting chemical analyses of garnet assemblages in kimberlites and their trains.

However, more reliable reconstruction of natural weathering processes requires studying the behavior of garnets in organic acids. Dissolution of silicate minerals in natural solvents, such as organic acids, was discussed in many publications (e.g., Energlyn and Brealey, 1971; Drever and Stillings, 1997; Zhang and Bloomb, 1999). According to Zhang and Bloomb (1999), the dissolution rates of most minerals are promoted by the presence of proton- and complex-forming ligands. They measured dissolution rates at different concentrations of citric, oxalic, and polygalacturonic acids at pH 4.0 and observed preferential release of Al, Fe, and Mg relative to Si. The experiments of Zhang and Bloomb (1999) showed that all ligands accelerated dissolution to rates increasing with solution concentrations of organic acids, and that the strengths of organic acids to promote dissolution was related to the strength of the metal–ligand complex formed in solution or on the mineral surface.

Drever and Stillings (1997) studied dissolution of silicate minerals (feldspars) in organic acids and revealed several mechanisms of their effect on mineral weathering rates, among which forming complexes with cations at the mineral surface. However, this mechanism is subject to effects of many other factors (solution pH, porosity of the dissolved material, etc.)

Earlier studies by Neuberger (Energlyn and Brealey, 1971) demonstrated that aminoacids could dissolve some minerals at pH close to that in natural environments where proton-forming ligands are limited while dissolution occurs by forming complexes. Sodic salts of aminoacids, nucleic acids, and nucleotides, present in all biotic objects, were also found to dissolve many minerals.

Inasmuch as our experiments aimed at reproducing natural LWP dissolution of garnets, the authors of the present research chose adenosine-triphosphate disodium salt (ATP- Na_2) as an etchant. This is a colorless or yellowish liquid, an organic solvent abundant in all biological systems and soils, which produces solutions with pH \sim 7, stable for several months (Zhang and Bloomb, 1999). The authors of the present research used the (ATP- Na_2) solution for medical injections. Its effect on garnets is much weaker and does not allow quantitative estimates of dissolution rates, though the etch surface patterns it forms in reasonable time are very similar to the natural ones and to those obtained by laboratory dissolution in HF.

Methods

The etching tests for estimating dissolution rates were applied to 233 pyrope grains from kimberlite. The grains were selected in water because the immersion medium can highlight their true color. Thus, the authors selected 2 to 4 mm pyropes of all colors from pale orange to dark violet, visually homogeneous, free from cracks or large inclusions.

Each grain was weighed and then placed in 10% HF. The weight loss was monitored by weekly weighing, for which the solution was removed, the grains were rinsed and air dried, and then placed back into the vial with a fresh 10% HF solution. Some grains developed fluoride crusts easily removable with a needle. The total etching time was six weeks (42 days).

At the final step of the experiment, 226 pyropes were analyzed for chemistry by the standard EMPA method. Seven grains underwent heavy corrosion fracture (Afanasiev et al., 2001, 2010) and were discarded. In total 71 grains out of 233 experienced fracture in the course of the tests. Five grains were analyzed in their core and rim and showed a homogeneous chemical composition.

To study the behavior of pyropes in organic solvents, the authors selected eleven 2-4 mm crystals from kimberlite. The crystals were rinsed ultrasonically in 2% HCl for 15 minutes, air dried, placed into polymer vials and soaked in the initial 7% (ATP-Na₂), pH 7.2, for three or four months. Then the solution was removed, the crystals were rinsed with water and air dried, and their surfaces were examined with a scanning electron microscope; after that the grains were again soaked in the initial solution. The total experiment duration was about eighteen months.

Results

The pyropes etched in HF exhibited prominent traces of dissolution (Fig. 1) identical to those (Fig. 3) in naturally occurring weathered garnets from lateritic provinces (Afanasiev et al., 2001, 2010). Dissolution produced either negative (pits, scratches, etch channels, or grooves) or positive (mammilla-like hillocks) structures on grain surfaces. Some grains additionally experienced spallation of small flakes along zones of highest stress, also common to natural dissolution effects.

Etching in (ATP-Na₂) for eighteen months (Fig. 2) likewise produced pits and dislocations on grain surfaces; etch channels sometimes merged into grooves along closely spaced dislocations, or less often hillocks, all similar to natural dislocations (Afanasiev et al., 2001, 2010).

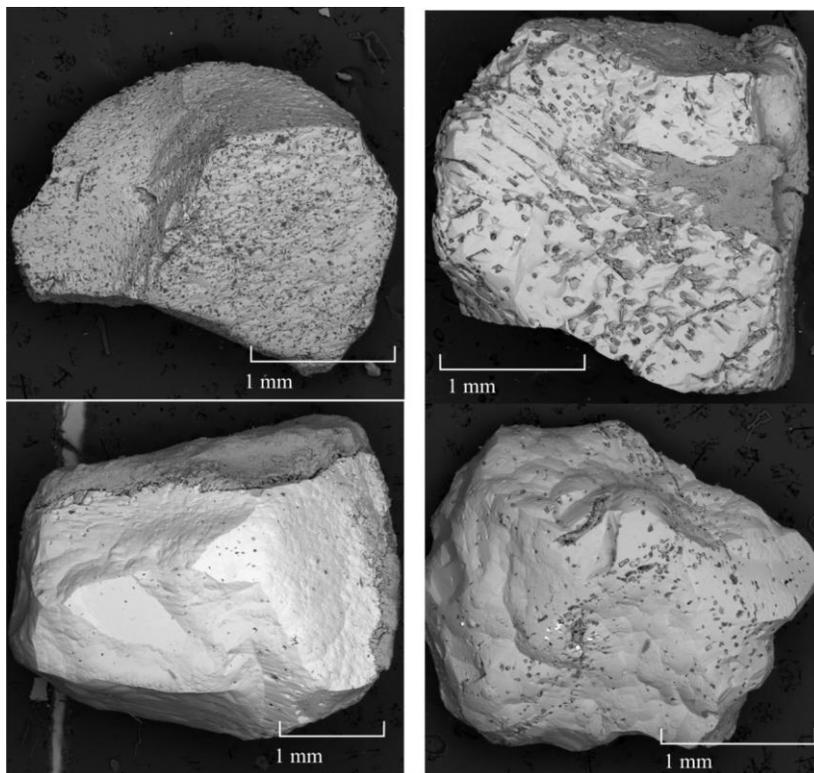


Fig. 1. Surface patterns in garnets produced by etching in HF for 28 days

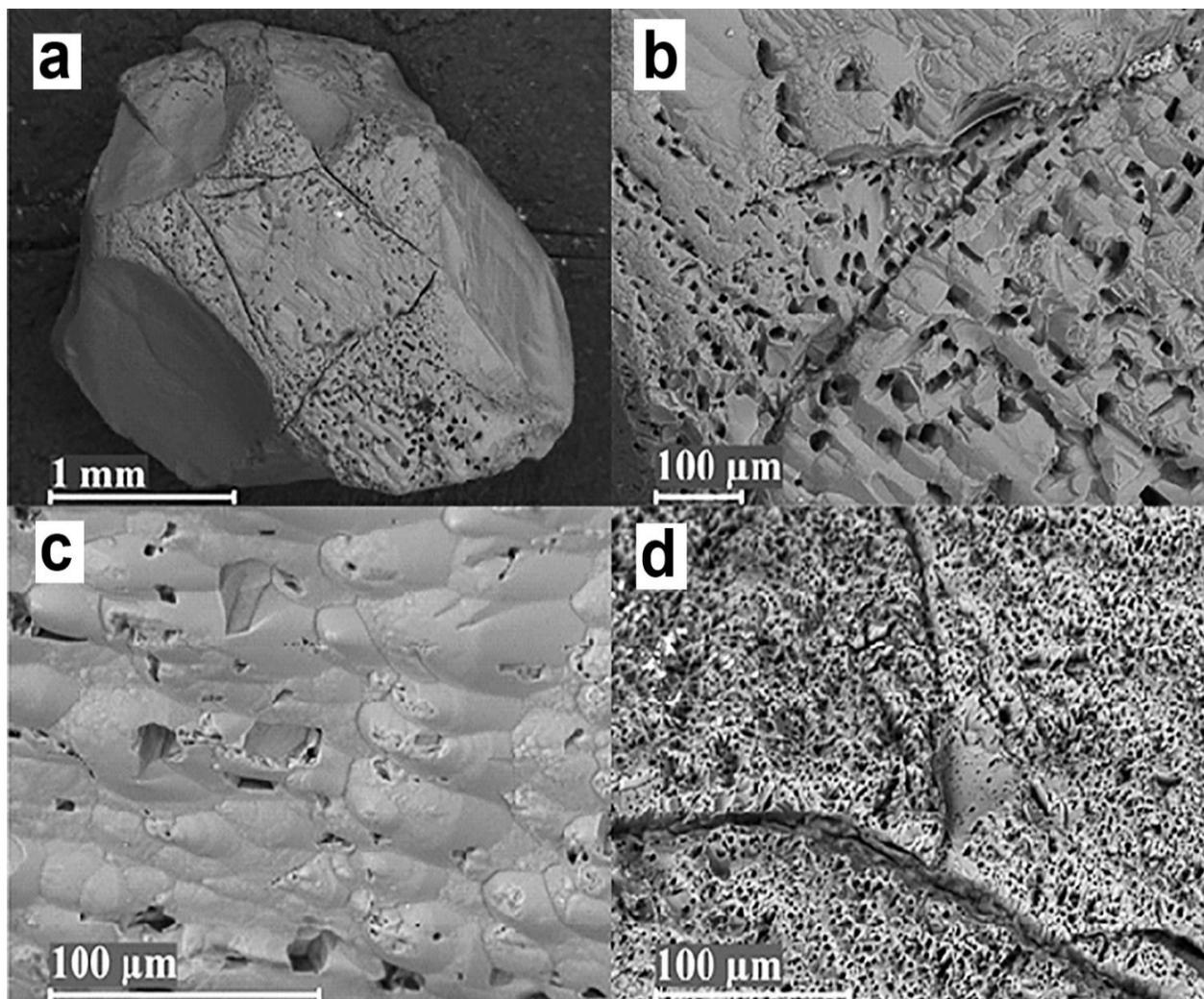


Fig. 2. Surface structures of garnets etched in 7% (ATP-Na₂) for 18 months. a: general view (crystal No. 9); b: wedge-shaped etch channels on an orange garnet (crystal No. 9); c: mamilla-like cuboid hillocks (surface of crystal No. 10); d: capillaceous etch channels on a violet garnet (surface of crystal No. 6).

In both cases, dislocation-controlled dissolution was predominant. The surfaces of most grains were densely cut by numerous etch channels along dislocations, sometimes arranged in chains corresponding to low-angle sub-grain boundaries (Afanasiev et al., 2001, 2010). Grooves formed mainly on pale (red or orange) pyropes while thin capillaceous channels developed most often on violet varieties.

The reported experiments showed that both ATP-Na₂ salt and HF acid can dissolve garnets to produce surface microtopography structures resembling those in their natural weathered counterparts and are thus suitable to model the chemical weathering process in kimberlitic garnets.

Figure 3 shows garnets from pre-Cenozoic sedimentary formations in different diamond provinces worldwide: Siberian craton (Yakutia), East European Platform (Arkhangelsk province), and Canada, as well as from a contemporaneous lateritic province in West Africa (Guinea). The similarity of surface patterns in garnets from different geographically dispersed areas prompts similarity also in their weathering conditions and history. The agreement between the laboratory and natural patterns (Figs. 1, 2, 3) means that the experiments were successful.

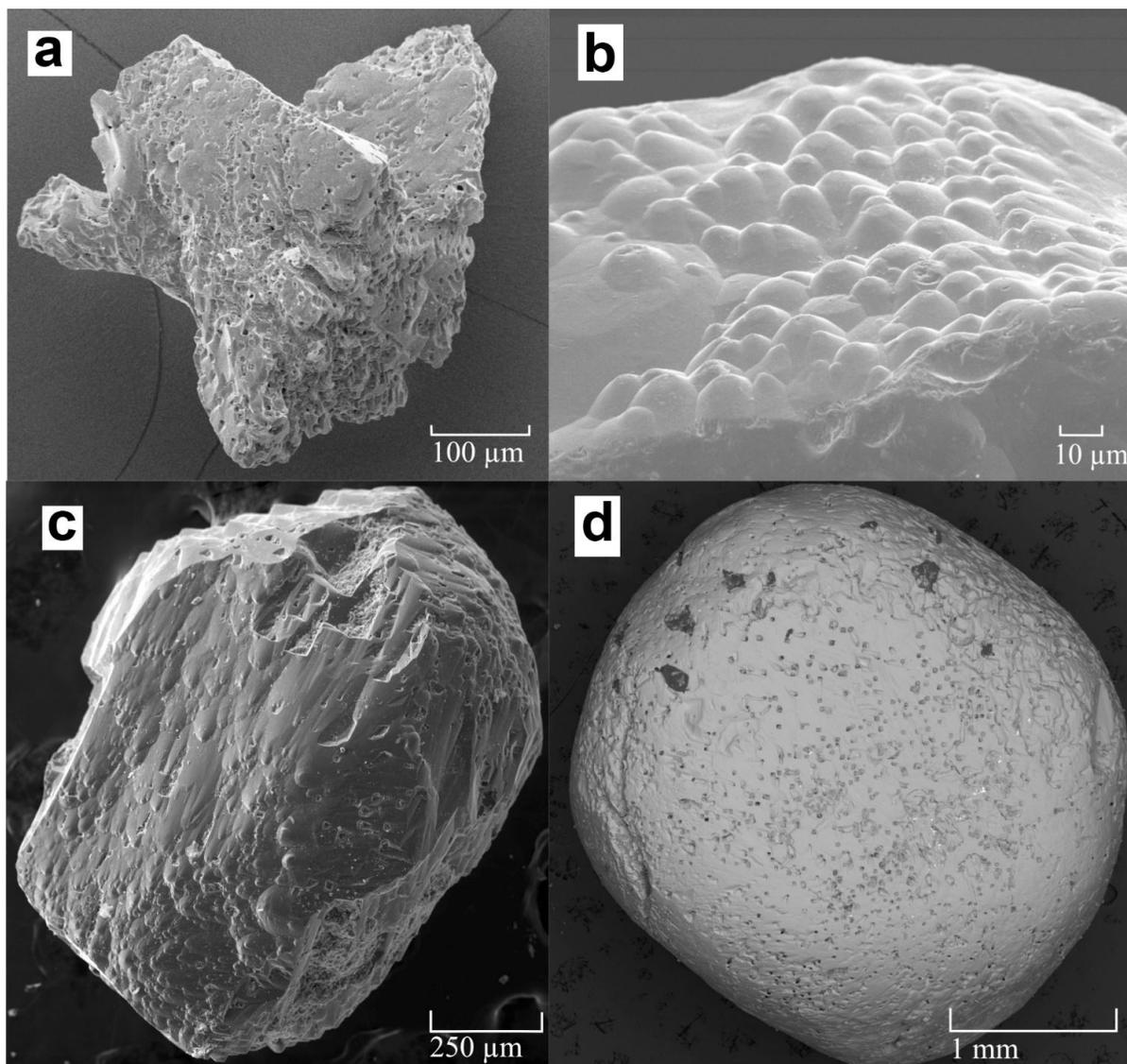


Fig. 3. Surface patterns of natural chemically weathered sediment-hosted garnets from different provinces. a: Arkhangelsk diamond province (1), b: Canada placers (1), c: weathered XXIII CPSU Congress kimberlite, d: West Africa (Guinea).

The similarity of surface patterns produced by etching in HF and (ATP-Na₂), which match well those in naturally occurring minerals from LWP, in spite of different dissolution mechanisms, may be due to the fact that dissolution follows structure defects in all cases. However, HF

providing much faster dissolution is better for laboratory tests than (ATP-Na₂) as it allows studying the dissolution behavior of minerals in a reasonably short time.

Chemical weathering may also show up as corrosion fracture (Afanasiev et al., 1984, 2001, 2010), which is often attendant with dissolution due to high surfactant activity of organic compounds. The latter adsorb on crystal surfaces, especially at higher-energy defect sites, thus bringing the crystal to a preferred energy state. Postmagmatic fracture in garnets is localized along defect zones (rhombohedral faces in garnet) and the fracture planes are flat, whereas weathering-produced cracks most often form conchoidal fracture as they follow randomly distributed remnant defects with lower excess energy (Afanasiev et al., 2001). Laboratory etching in HF can cause corrosion cracks in garnet as well, and that was the reason why some pyrope grains broke down into pieces and had to be discarded. This is another feature of similarity with the natural weathering effects.

The stability coefficient (K_y) per unit time (24 hr of etching), as the ratios of the original weight after 42 days of etching in HF to the output weight:

$$K_y = 1 - (1 - K_{42})/42, \text{ where } K_{42} = \text{weight}_{\text{final}} / \text{weight}_{\text{initial}}$$

Once the reaction stopped, dissolution rates of pyropes were analyzed as a function of their composition. The chemistry and, partly, color of kimberlitic garnets correlates with their paragenetic types, and it was reasonable to classify the analyzed pyropes according to their parageneses. The parageneses were identified using the classification of Schulze (2003), with reference to Sobolev's scheme (Sobolev et al., 1969, 1973) and its later modifications (Tychkov et al., 2008, 2018). Thus eight paragenetic groups and subgroups of eclogitic, megacryst, and peridotitic garnets were distinguished. Eclogitic (1) garnets have Cr₂O₃ < 0.5 wt. % and belong to groups A or B according to Schulze (2003). Garnet megacrysts (2) formed by fractional crystallization at the lithosphere-asthenosphere transition contain Cr₂O₃ (up to 5 wt. %), TiO₂, and FeO. Peridotitic garnets have Cr₂O₃ > 0.5 wt. % and are further subdivided into lherzolite (3) and harzburgite-dunite (4) parageneses (Sobolev et al., 1969, 1973; Pokhilenko and Sobolev, 1995). The latter include the graphite (4A) and diamond (4B) depth facies with different percentages of khorringite (Sobolev et al., 1969; Pokhilenko and Sobolev, 1995). Lherzolitic garnets are of three sub-types that differ in MnO and TiO₂ contents and crystallization temperatures (above or below 1100°C). The high-temperature enriched garnets in lherzolites (3C) (Brey and Kohler, 1990) often bear signature of deformation (or cataclasis) and secondary enrichment with asthenospheric material (Pokhilenko et al., 1999, 2015; Agashev et al., 2013; Howarth et al., 2014; Pernet-Fisher et al., 2015). The lower-temperature lherzolitic garnets include two depth sub-groups with different contents of Cr₂O₃, MgO, and CaO: those formed at relatively shallow depths (3A), under 4.3 GPa and 925°C (Tychkov et al., 2008, 2018) and deeper (3B). These *PT* parameters limit the stability field of diamond at a heat flux of 38 mW/m² (Kennedy and Kennedy, 1976).

The compositions of studied garnets that belong to different parageneses are plotted in the CaO-Cr₂O₃ coordinates (Fig. 4).

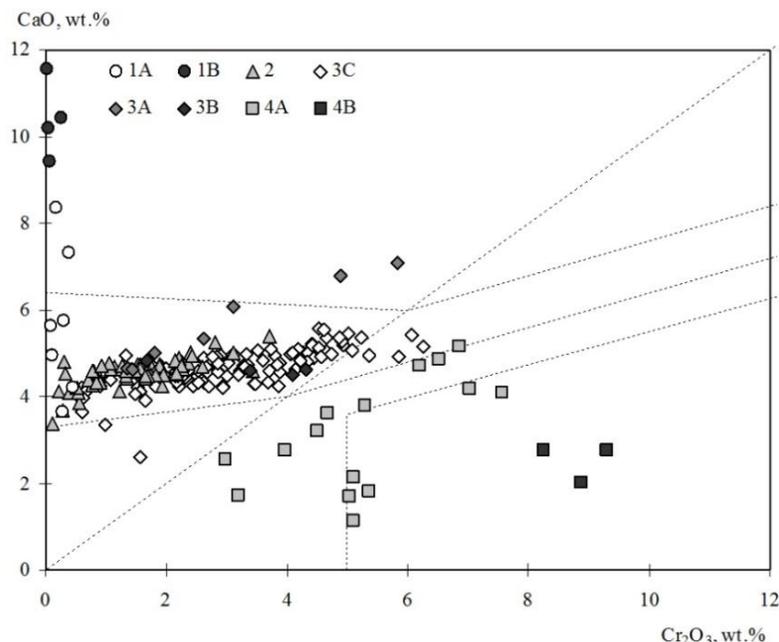


Fig. 4. Garnets of different parageneses in the CaO-Cr₂O₃ diagram (Sobolev et al., 1973b). Labeling of paragenetic groups is explained in text

The average stability coefficients (K_y) calculated for different garnet parageneses are listed in Table 1, together with average Cr₂O₃ and CaO contents. The parageneses are listed in the order of decreasing dissolution rates (increasing stability).

Table 1. Average stability coefficients K_y and Cr₂O₃ and CaO contents for different garnet parageneses

Paragenesis	n	K_y	Cr ₂ O ₃	CaO
1A	7	0.9906	0.26	5.67
2	68	0.9922	1.54	4.56
1B	4	0.994	0.10	10.41
3A	118	0.9946	2.93	4.65
3B	7	0.9946	3.00	5.65
3C	4	0.9964	3.36	4.64
4A	15	0.9973	5.29	3.16
4B	3	0.9988	8.81	2.51

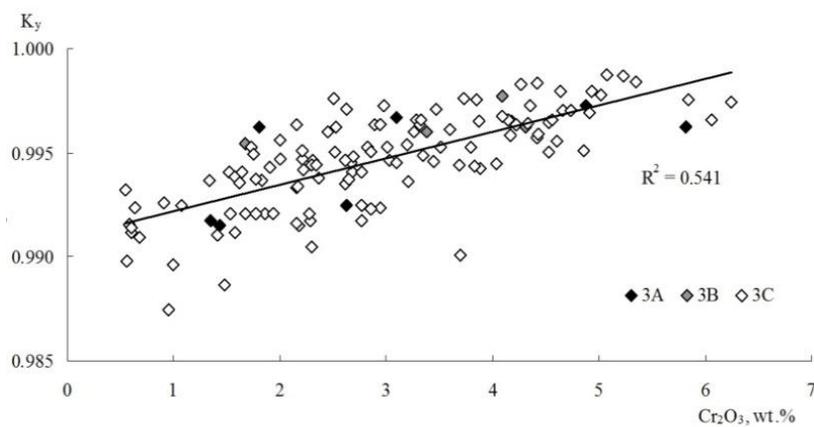
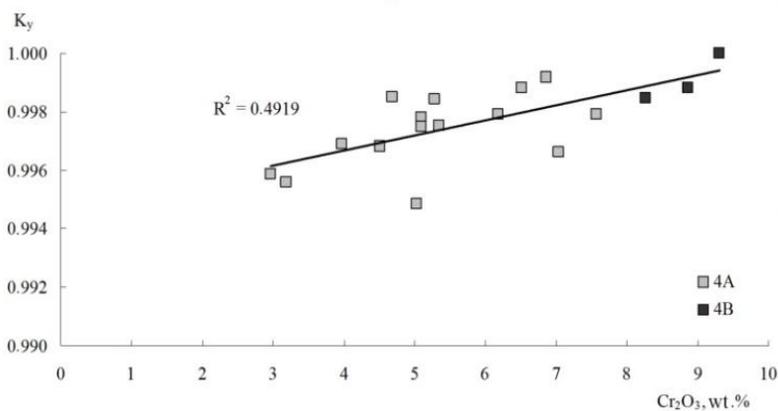
The dissolution rates increase proportionally to Cr₂O₃ decrease (Fig. 5, Table 1). Different parageneses make up a series of increasing dissolution rates (decreasing stability) as a function of Cr₂O₃: diamond facies harzburgite-dunite (4B) – graphite facies harzburgite-dunite (4A) – shallow lherzolite (3A) – deep lherzolites of depleted (3B) and secondary enrichment (3C) compositions – megacrysts (2) – type A eclogites (1A). Garnet of the eclogite B paragenesis (1B) makes an exception, with its average stability being as high as 0.9940 at very low Cr₂O₃, which is notably higher than in megacrysts and group 1A eclogites with higher contents of Cr₂O₃; yet, the group contains the highest amount of Ca which becomes the main stability factor (see below).

The stability coefficients plotted against Cr_2O_3 separately for each paragenesis (Fig. 5) show good correlation for harzburgitic and lherzolitic garnets and a worse but quite significant correlation for megacrysts, with correlation coefficients $r = 0.7, 0.74,$ and $0.48,$ respectively (Table 2).

Table 2. Correlation between stability coefficients (K_y) and major oxides, quoted as average contents with standard deviation, for the whole sample and separately for different parageneses

		Si O ₂	Ti O ₂	Al ₂ O ₃	Cr ₂ O ₃	F e O	Fe ₂ O ₃	M n O	M g O	C a O	N a ₂ O	Al m	S p e s	A n d	Ti A n d	G r o s	U v a	K n o	Py r
Average value	4	42.29	0.11	19.32	5.88	5.54	0.74	0.34	22.55	3.05	0.05	11.06	0.69	1.98	0.28	0	5.81	10.77	69.4
	3	42.34	0.31	20.84	2.95	6.05	1.20	0.33	21.06	4.70	0.07	12.09	0.67	3.22	0.83	1.28	7.00	1.31	73.6
	2	42.34	0.75	20.86	1.54	6.44	2.12	0.29	20.82	4.56	0.10	12.91	0.59	5.67	2.00	1.06	3.44	0.89	73.44
	1	41.69	0.33	22.45	0.20	9.24	1.04	0.25	16.95	7.41	0.12	18.79	0.59	2.82	0.88	15.56	0.77	0	60.87
	Total	42.31	0.43	20.81	2.62	6.22	1.43	0.32	20.91	4.66	0.08	12.58	0.64	3.84	1.14	1.81	5.52	1.87	72.6
Standard deviation	4	0.54	0.13	1.48	1.83	0.44	0.19	0.04	1.19	1.21	0.02	0.88	0.08	0.05	0.35	0	2.79	5.16	6.01
	3	0.36	0.15	1.02	1.33	0.83	0.29	0.04	0.73	0.52	0.02	1.68	0.08	0.07	0.39	1.77	2.45	1.91	3.19
	2	0.31	0.18	0.74	0.76	0.90	0.63	0.04	0.65	0.31	0.02	1.87	0.09	1.06	0.47	1.53	1.82	1.03	1.98
	1	0.70	0.23	0.46	0.15	1.93	0.23	0.09	3.35	2.75	0.06	4.22	0.17	0.06	0.64	8.21	0.42	0	10.91
	Total	0.41	0.27	1.11	1.73	1.16	0.62	0.05	1.43	1.10	0.03	2.40	0.10	1.06	0.72	3.91	2.96	3.37	4.83
Correlation	4	-0.57	0.42	-0.72	0.70	0.68	-0.06	0.69	-0.43	0.32	0.76	0.74	-0.40	0.23	-	-	0.46	0.47	-0.76
	3	-	-	-	0.7	-	0.1	0.	-	0.	-	0.	0.	-	-	-	0.	0.	-

	0.33	0.07	0.74	4	0.15	6	14	0.30	51	0.12	0.13	17	17	0.06	0.57	65	62	0.53
2	-0.06	-0.07	-0.25	0.48	0.04	-0.18	0.34	-0.21	0.15	-0.08	0.06	0.36	-0.18	-0.07	-0.20	0.43	0.24	-0.27
1	-0.78	0.16	-0.59	-0.21	0.054	-0.26	-0.023	-0.078	0.83	0.41	0.56	-0.22	-0.22	0.18	0.78	-0.19	-	-0.79
Total	-0.18	-0.43	-0.61	0.75	-0.222	-0.38	0.39	0.07	0.00	-0.36	-0.20	0.41	-0.38	-0.42	-0.24	0.62	0.55	-0.28



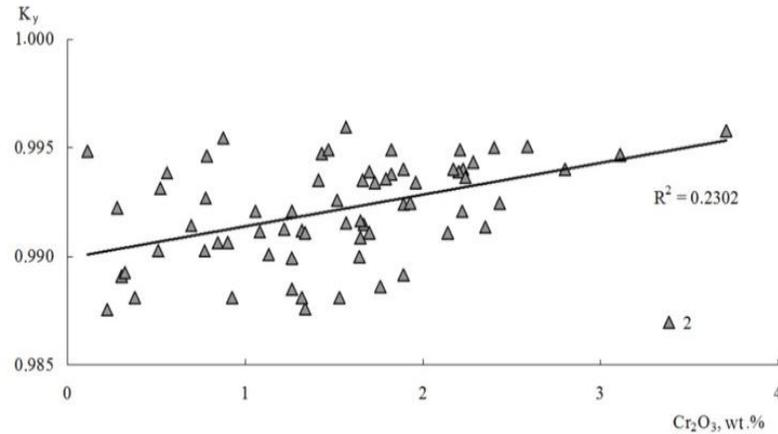


Fig. 5. Stability coefficient as a function of Cr_2O_3 in harzburgite-dunite (4A and 4B), lherzolite (3A, 3B, 3C), and megacryst (2) garnets

Note that the host rocks of megacrysts and enriched garnets underwent both ductile and brittle deformation in the zone of lithosphere-asthenosphere interaction synchronously with kimberlite magmatism (Pokhilenko et al., 1999, 2015; Agashev et al., 2013; Howarth et al., 2014), which increased the density of dislocations in garnets and, hence, reduced their chemical stability. Garnets of the eclogitic groups A and B (with low $Cr_2O_3 < 0.5$ wt. %) demonstrate weak inverse proportionality between stability and Cr_2O_3 contents, with $r = -0.21$. That is, the dissolution rates of low- Cr_2O_3 garnets rather depend on CaO, and their stability increases with CaO, at $r = 0.83$ (Fig. 6).

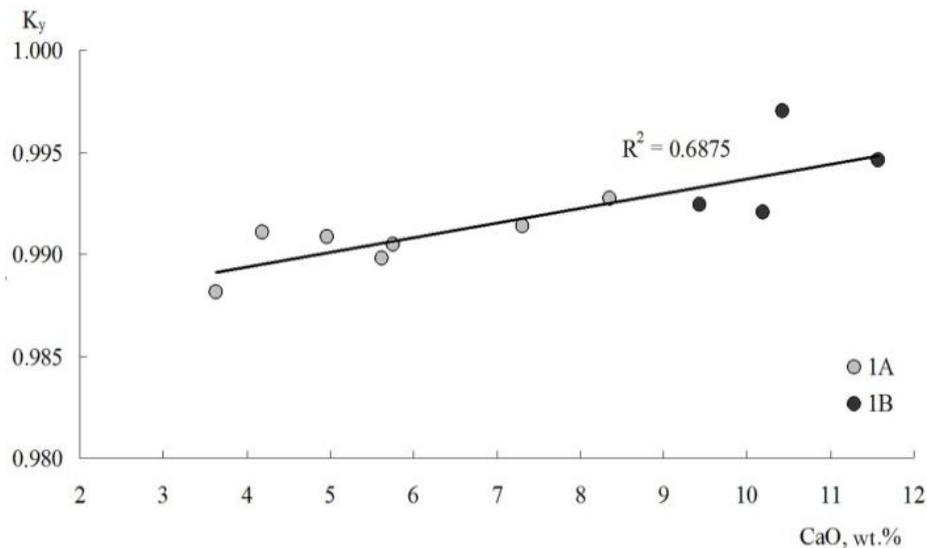


Fig. 6. Stability coefficient as a function of CaO in eclogitic garnets

Average dissolution rates (residual weight) are plotted for each paragenetic group in Fig. 7.

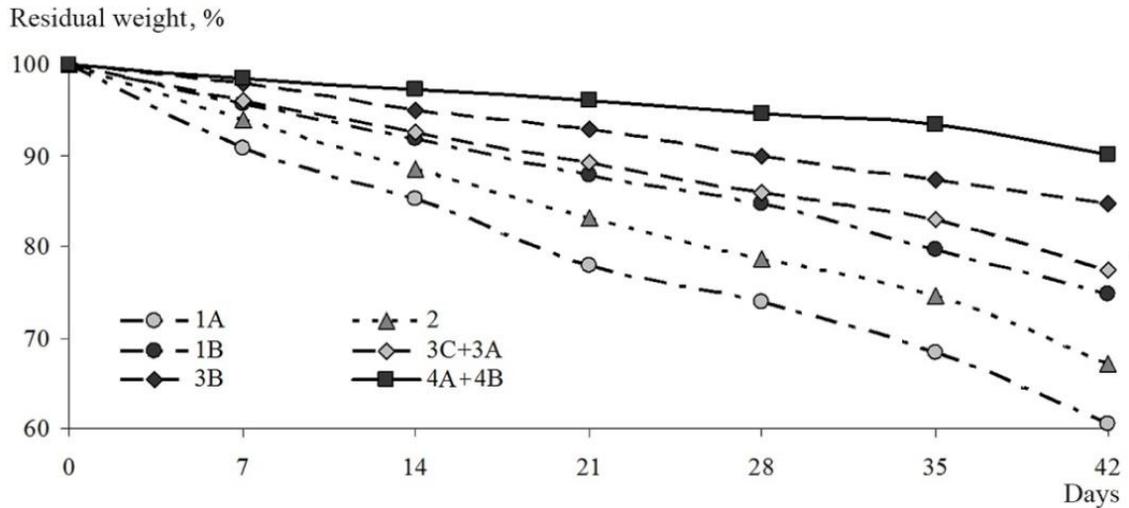


Fig. 7. Chemical stability (dissolution rates) of garnets of different parageneses etched in HF

Table 2 shows correlation between chemical stability (dissolution rates) and contents of major oxides quoted as average values with standard deviation, for the whole sample and for each paragenesis. The contents of Al_2O_3 , CaO and FeO increase while MgO, Cr_2O_3 and MnO decrease in the series of ‘harzburgite-dunite – lherzolite – megacryst – eclogite’ parageneses. The percentages of endmember minerals behave correspondingly, namely almandine and grossular increase while knorringite and spessartite decrease (Table 2).

In search for additional controls on the stability of garnets to chemical weathering, the authors investigated dependence of dissolution rates on unit cell size (a_0). The unit cell edge length of garnets can be derived from their compositions using linear relationships suggested by different authors:

$$a_0 = 9.125 + 1.56 * R^{2+} + 2.0 * R^{3+} \text{ after (Gnevushev et al., 1956);}$$

$$a_0 = 9.223 + 1.407 * R^{2+} + 1.694 * R^{3+} \text{ after (Bertaut and Forrat, 1957);}$$

$$a_0 = 9.90 + 1.212 * R^{2+} + 1.464 * R^{3+} \text{ after (McConnel, 1966);}$$

where R^{2+} and R^{3+} are the average radiuses of bivalent and trivalent cations, respectively.

$$R^{2+} = W_{Fe2} * R_{Fe2}^{2+} + W_{Mn2} * R_{Mn2}^{2+} + W_{Mg2} * R_{Mg2}^{2+} + W_{Ca2} * R_{Ca2}^{2+} + W_{Na} * R_{Na}^{2+}$$

$$R^{3+} = W_{Fe3} * R_{Fe3}^{3+} + W_{Ti3} * R_{Ti3}^{3+} + W_{Cr3} * R_{Cr3}^{3+} + W_{Al3} * R_{Al3}^{3+}$$

W is the fraction of each element (in atomic weight) relative to 100%.

The parameters R^{3+} and R^{2+} were estimated in this study with reference to the ion radius values reported by Bokiy (1971). Inasmuch as most of the ionic compounds have a coordination number (c.n.) of 6, all ion radius sizes are quoted for c.n. = 6. The trivalent cations in the garnet structure have c.n. = 6, and need no correction. However, the ion radiuses of the bivalent cations with c.n. = 8 include a correction of +3% (Bokiy, 1971). With the above relationships, the unit cell sizes a_0 were calculated for all pyrope grains used in the experiments.

Additionally, the authors of the present research made unit cell size and refractive index (N_0) calculations based on the diagram of Winchell (1958). As it was shown previously (Sobolev et al., 1973a; Lazko, 1979), the error in the compositions of garnets reproduced using Winchell's diagram is within 3% for main garnet varieties. The authors applied the diagram to derive a_0 and N_0 for garnet, grossular, almandine, andradite, and uvarovite. The samples were divided into eclogitic (1A, 1B), megacryst (2), lherzolite (3A, 3B, 3C), and dunitite-harzburgite (4A, 4B) paragenetic groups, in a generalized way without division into subtypes, and are referred to below as 1, 2, 3 and 4, respectively.

The calculated average values of a_0 , K_y , and CaO and Cr_2O_3 contents are listed in Tables 3 and 4, separately for different garnet groups. In the series 4 – 3 – 2 – 1, the major oxides Al_2O_3 , CaO, and FeO increase while MgO, Cr_2O_3 , and MnO decrease. Correspondingly, the average R^{3+} radiuses become ever smaller, because Cr^{3+} is larger than Al^{3+} and Fe^{3+} ; the R^{2+} ones, on the contrary, become larger as the Ca^{2+} and Fe^{2+} cations are much larger than Mg^{2+} . The unit cell sizes increase from harzburgitic to eclogitic garnets.

Table 3. Average values of R^{3+} and R^{2+} cation radius, unit cell edge length (a_0) in Angström units, and refractive index (N_0), as well as calculated coefficients of correlation between these values and stability of garnets (K_y), for the whole statistical sample and for each group. Abbreviations for parageneses are the same as in text. Numerals in parentheses refer to calculations with equations from Gnevushev et al., 1956 (1), Bertaut and Forrat, 1957 (2), McConnel, 1966 (3), and Winchell, 1958 (4).

		Number of grains	R^{3+}	R^{2+}	a_0 (1)	a_0 (2)	a_0 (3)	a_0 (4)	N_0 (4)
Average values	Total	286	0.580	0.809	11.547	11.354	11.730	11.535	1.748
	H	31	0.583	0.795	11.532	11.340	11.718	11.513	1.746
	L	150	0.580	0.808	11.546	11.353	11.729	11.536	1.748
	MC	82	0.581	0.808	11.548	11.355	11.730	11.536	1.750
	E	23	0.574	0.832	11.572	11.377	11.750	11.555	1.745
Correlation coefficient	Total	286	0.56	-0.06	0.16	0.15	0.15	0.07	0.24
	H	31	0.75	0.45	0.65	0.64	0.64	0.43	0.50
	L	150	0.74	0.52	0.69	0.69	0.69	0.67	0.67
	MC	82	0.16	0.21	0.21	0.21	0.21	0.24	0.27
	E	23	0.2	0.74	0.76	0.75	0.75	0.76	0.55

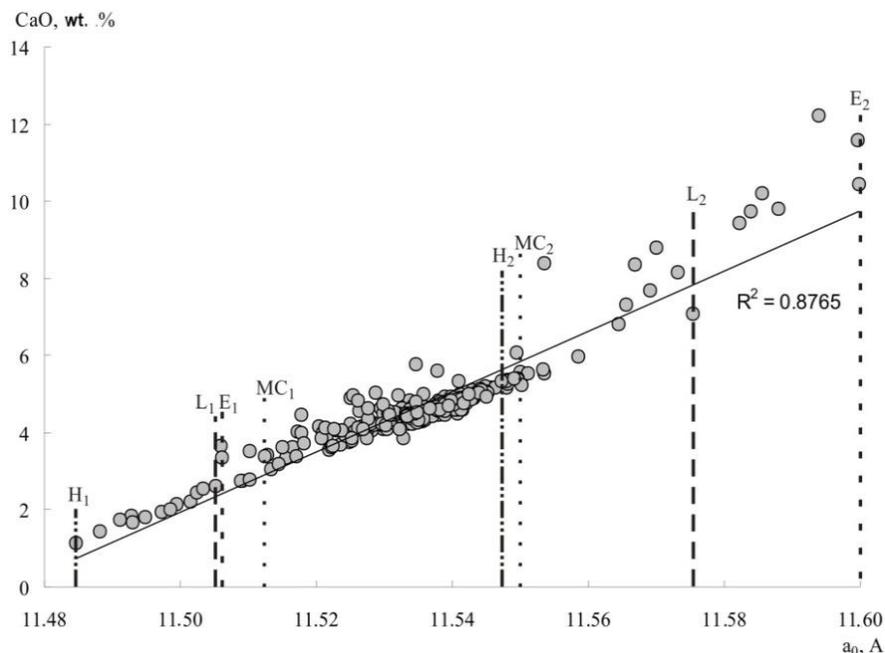


Fig. 8. Unit cell size (a_0) vs. CaO contents in garnets ($n=286$); solid line is function approximation; dash line and Abbreviated names of parageneses bound the beginning (1) and end (2) of the respective zones

The chemical stability and Cr_2O_3 correlate well within the groups of harzburgitic, lherzolitic, and megacryst garnets, but the stability of eclogitic garnets depends more on the CaO content. On the other hand, the calculated unit cell sizes of garnets correlate with CaO wt.% to more than $r = 0.91$ (Fig. 1), because Ca^{2+} has a large ion radius (30% larger than Fe^{2+}).

The results demonstrate that the chemical stability of garnets within each paragenetic group increases with the unit cell size, which correlates with CaO; the correlation is strong in eclogitic and lherzolitic garnets and moderate in harzburgitic and megacryst varieties (the correlation coefficients are listed in Table 3). On the other hand, the relationship is inverse between groups: the stability decreases from harzburgite-dunitic to eclogitic garnets as the unit cell size increases.

Discussion

The reported experimental data on etching of garnets in HF and (ATP-Na_2) perfectly approximate the naturally occurring patterns in garnets exposed to chemical weathering in laterite profiles but differ from dissolution patterns in other settings (Afanasiev et al., 2001, 2010).

The weight loss monitoring and subsequent EMPA analysis show that the contents of CaO and Cr_2O_3 control the stability of garnets to chemical weathering (Table 4). Namely, megacrysts and lherzolitic garnets become more stable with Cr_2O_3 increase (from 1 to 6 wt.%), CaO being little variable (4-5.5 wt. %). Garnets with low CaO (<4 wt.%), such as the harzburgite-dunitic paragenesis, likewise tolerate weathering if Cr_2O_3 is high. The chemical stability increases with CaO increase from 3.5 in eclogitic garnets of group A to 12 wt.% in those of group B, at $\text{Cr}_2\text{O}_3 <$

0.5 wt. %. Note that the analyzed grains did not include green uvarovite pyropes high in both CaO and Cr₂O₃ contents, but they demonstrated the lowest dissolution rates (almost no weight loss) in our previous qualitative experiments (Afanasiev et al., 1984, 2001). Correspondingly, crustal garnets with very low CaO and Cr₂O₃ can be expected to be the least stable to chemical weathering (Spetsius, Serenko, 1990, Stowell et al., 2010).

Table 4. Average stability coefficients (K_y), Cr₂O₃ and CaO contents for garnets of different groups. Abbreviations for parageneses are the same as in text

Paragenesis	Number of grains	K_y	Cr ₂ O ₃ , wt.%	CaO, wt.%
1A	18	0.619	0.25	6.40
2	82	0.680	1.57	4.52
1B	5	0.730	0.11	10.29
3	150	0.775	2.96	4.67
4	31	0.888	5.58	3.07

Thus, the dissolution rates and chemical stability of garnets exposed to chemical weathering depend mainly on CaO at low Cr₂O₃ in eclogitic parageneses and on Cr₂O₃ in peridotitic high-Cr garnets from lherzolite and harzburgite-dunite.

The discovered dependence of garnet stability on CaO and Cr₂O₃ contents, correlated with color, may interfere with diamond prediction because garnets in placer assemblages have higher Cr contents than their counterparts from the primary deposits. Unfortunately, the changes caused by chemical weathering to garnet assemblages have never been quantified to reconstruct their primary compositions. Known are only the general trends of increasing average Cr enrichment in KIM trains relative to the primary kimberlites (Afanasiev et al., 2001, 2013b).

Our earlier attempts of reconstructing the primary compositions of garnet assemblages (Afanasiev et al., 1984, 2010) by excluding the most strongly variable low-Cr varieties from the analyzed sample of grains failed because each kimberlite body turned out to have its own “truncation level” according to Cr₂O₃ contents, and no universal criterion could be applied. It has become clear now that further experimental studies of the discussed phenomenon are indispensable for mitigating the related diamond prediction problems.

Conclusions

The reported experimental results demonstrate that kimberlitic garnets are dissolved by both HF and (ATP-Na₂) developing grain surface patterns that perfectly match those observed in naturally occurring garnets exposed to chemical weathering in laterite profiles. The contents of calcium and chromium oxides are the principal controls of dissolution rates and, hence, the stability of garnets to chemical weathering: CaO for the low-Cr eclogitic garnets and Cr₂O₃ for the high-Cr peridotitic varieties (lherzolite and harzburgite-dunite parageneses). These results highlight main trends in the composition of mineral assemblages in lateritic provinces.

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Paragenetic analysis of garnets: *Nikolay S. Tychkov, Nikolay P. Pokhilenko*.

Discussion, conclusions: *Valentin P. Afanasiev, Oleg V. Snegirev, Olga A. Kozmenko, Nikolay S. Tychkov, Nikolay P. Pokhilenko*

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