

Dehydration of Serpentinized Ultramafic Rocks as a Candidate Deep Crustal Source of Natural Hydrogen and Hydrocarbons: Experimental Evidence from the Lesser Caucasus

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Abstract

Natural hydrogen generated by serpentinization — the hydration of ultramafic rocks, in which ferrous iron is oxidised and molecular hydrogen is liberated from water — has recently been shown to proceed at rates of only 0.1 to 0.5 tonnes $\text{H}_2 \text{ yr}^{-1} \text{ km}^{-3}$ of reactive rock, implying that economically significant accumulations would require 10^3 to 10^4 years to develop [1]. A complementary process capable of releasing fluid abruptly, rather than gradually, would relax this constraint.

This paper reports experimental evidence for such a process: the dehydration (deserpentinization) of already-serpentinized ultramafic rocks carried to greater crustal depths. Serpentinites and serpentinized ultramafic rocks of the ophiolite belts of the Lesser Caucasus were studied at pressures to 20 kbar, and at $5\text{--}6 \times 10^8$ Pa with heating to 900 °C, in solid-media apparatus with continuous monitoring of compressional-wave travel time [2, 3].

Dehydration proceeds over the interval 500–700 °C, the interval differing between samples (550–700 °C and 600–750 °C in the two apoperidotite serpentinites) according to serpentine variety, serpentine content and rock fabric, and is accompanied by step-like changes in wave velocity and by volume changes reaching 30%. Petrographic and X-ray diffraction analysis records the breakdown of chrysotile, lizardite, antigorite and brucite to forsterite and enstatite, with redistribution and recrystallization of magnetite and the formation of iron hydroxides. Iron and chromium oxides constitute 5–8% of serpentinized ultramafic rocks throughout the belts. Gas chromatographic analysis of the released fluid identified alkanes in both fractions: the first fluid sample contained low-molecular-weight alkanes $\text{C}_{16}\text{--}\text{C}_{21}$ with a maximum at C_{20} , while the second was dominated by high-molecular-weight alkanes $\text{C}_{23}\text{--}\text{C}_{35}$ with trace C_{45} [4].

Molecular hydrogen was not measured. The experimental programme was conducted before natural hydrogen became a subject of interest, and no gas analysis for H_2 was performed. Hydrogen is identified here as a predicted product of the reaction on mineralogical and thermodynamic grounds, and its measurement is the principal outstanding requirement.

Serpentinized ultramafic rocks exhibit densities of 2.53–2.77 g/cm^3 and compressional velocities of 5.05–5.77 km/s, against 2.98–3.19 g/cm^3 and 6.45–7.43 km/s for unaltered pyroxenites, permitting buried serpentinized bodies to be identified as low-velocity, low-density layers. Such layers were predicted at 35–50 km beneath Armenia from laboratory data in 1975 [5] and have since been repeatedly detected on deep seismic sounding profiles [6, 7]. Implications for hydrogen exploration in orogenic belts containing relics of palaeo-oceanic lithosphere are discussed.

Keywords: natural hydrogen; geologic hydrogen; deserpentinization; dehydration; serpentinite; ophiolite; Lesser Caucasus; high-pressure experiment

1. Introduction

Naturally occurring molecular hydrogen is now the subject of substantial international exploration activity, and the principal constraint on the development of the resource is recognised to be geological rather than technological: the difficulty lies in predicting where hydrogen is generated at depth, and whether it migrates and accumulates in producible quantities.

Serpentinization is considered one of the principal mechanisms of natural hydrogen generation. In this reaction, ferrous iron in primary minerals is oxidised to ferric iron in secondary phases, and the hydrogen of water is thereby reduced to H_2 [1]. Maximum rates occur between 200 °C and 300 °C, and the reaction also lowers the density and seismic velocity of the host rock.

1.1 The kinetic constraint

Recent quantitative work has, however, identified a difficulty with this model as a source of economic accumulations. Christiansen and co-authors [1], combining three-dimensional geophysical inversion with numerical modelling of fluid-rock processes in the fertile lherzolites of the Western Pyrenees and the depleted harzburgites of Northern California, constrain hydrogen generation to approximately 0.1–0.5 tonnes H_2 yr^{-1} km^{-3} of reactive rock, with total production of some 300–600 tonnes H_2 yr^{-1} . They find the rate limited by hydrogen saturation in the fluid and by reaction kinetics, and conclude that generation in mantle-derived serpentinization systems proceeds slowly, making rapid large-scale replenishment unlikely and implying that economically relevant accumulations would require thousands to tens of thousands of years to develop.

This is a significant constraint. A process that liberates fluid abruptly, over short geological intervals rather than continuously over millennia, would not be subject to it.

1.2 A second difficulty: inherited alteration

A separate question concerns serpentinized ultramafic bodies exposed within continental orogenic belts. In the majority of cases these are tectonically emplaced relics of oceanic lithosphere, and their serpentinization was accomplished by ocean water, in an oceanic setting, before emplacement. Attributing their alteration to meteoric infiltration at their present location misidentifies an inherited feature as a local one, and in consequence misplaces both the depth and the timing of hydrogen generation.

1.3 Scope of this paper

This paper addresses what occurs when serpentinized ultramafic rock, produced in the oceanic environment and subsequently incorporated into continental crust, is carried to depths at which it becomes thermally unstable and dehydrates. The experimental programme reported here was conducted at the Laboratory of Experimental Seismotectonics, Yerevan, established in 1970 under Academician A. T. Aslanyan. Dehydration under simultaneous high pressure and temperature was first modelled in that laboratory in 1987 and reported in 1988 [2].

2. Geological setting

Armenia lies within the Lesser Caucasus meganticlinorium, characterised by deep faults and flexures and by intensive intrusive and effusive magmatism. Three ophiolite belts are recognised — the Sevan-Akera, the Vedi and the Zangezur [3] — comprising basic and ultrabasic rocks and their metamorphosed varieties, representing relics of oceanic lithosphere incorporated into continental crust during the closure of Tethyan oceanic domains.

Interpretation of the crustal section indicates a serpentinized layer at the base of the crust at depths of 35–50 km, characterised by reduced seismic velocity, low density, high plasticity and elevated magnetization [5,

8]. This layer was first proposed on the basis of laboratory measurements of elastic properties combined with the deep seismic surveys carried out in Armenia in 1973–74 [5].

3. Materials and methods

3.1 Samples

Samples were collected from the ophiolite belts and comprise serpentinites of apoperidotite, apodiabase and apolherzolite parentage, serpentinized peridotites, harzburgite, wehrlite, pyroxenites, garnet-pyroxene rocks, gabbro-norite, amphibolite, diabase and quartz diorite. More than 150 varieties of mafic and ultramafic rock were examined over the course of the programme. Two sample geometries were used: cylinders of 12 mm height and 12 mm diameter for the experiments involving heating, and cylinders of 20 mm height and 20 mm diameter for the measurements made at pressure without heating.

3.2 Apparatus and sample assembly

Measurements were performed in solid-media high-pressure apparatus (Figure 1). The sample was enclosed between graphite washers and dolomite cylinders, surrounded by a graphite heater and dolomite sleeves, with a thermocouple mounted in a dolomite insert adjacent to the sample, pressure being transmitted through the assembly by a punch. The graphite envelope served as the heating element and the dolomite as the pressure-transmitting medium.



Details of the sample for investigation at high thermobaric conditions

Figure 1. Assembly of the sample for investigation at high thermobaric conditions. From top: dolomite cylinder; graphite washer; sample; graphite washer; dolomite cylinder carrying the thermocouple; graphite heater; dolomite sleeves; thermocouple; punch.

3.3 Experimental conditions

Compressional- and shear-wave velocities and densities were determined at pressures to 20 kbar at room temperature [3]. Dehydration behaviour was investigated at $5\text{--}6 \times 10^8$ Pa with progressive heating to 900 °C [2]. In the latter regime, pressure was first raised at room temperature to 5×10^8 Pa to establish contact between sample and assembly; temperature was then raised progressively at constant applied load, pressure

in the chamber rising correspondingly. Electronic instrumentation permitted continuous monitoring of compressional-wave travel time throughout, with registration of length change and hence volume change.

3.4 Analytical methods

Petrographic examination of thin sections was carried out before and after each experiment, and mineral phases were identified by X-ray diffraction. The fluid phase released during dehydration was collected in the apparatus and analysed by gas chromatography at the Institute of Oceanology, Moscow [4].

The gas chromatographic analysis was directed at hydrocarbon components. No analysis for molecular hydrogen was performed, hydrogen not being a subject of interest at the time. See Section 7.

3.5 Apparatus provenance and measurement parameters

The high-pressure apparatus operating to 20 kbar was developed before 1970 at the Laboratory of High Pressures, Institute of Physics of the Earth of the Academy of Sciences, under the direction of Professor M. P. Volarovich. The apparatus used for the experiments involving heating, operating to 8–10 kbar and 1000 °C, was built at the Laboratory of Experimental Seismotectonics of the Polytechnic Institute, Yerevan, in 1980. The dehydration experiments reported here were conducted at 5–6 kbar, within that range.

Parameter	Value
Measurement precision	5–7%
Ultrasonic frequency	1 MHz
Transducers	STS-19
Gas chromatograph	SS-50

The thermocouple type is not recorded in the surviving documentation. The chromatograph is reported by the investigator as an SS-50 instrument.

4. Results

4.1 Density, porosity and elastic wave velocities

Densities, porosities, modal compositions and wave velocities for representative ultramafic rocks are given in Table 1. A systematic contrast is evident. Serpentinized lherzolite, serpentinized peridotites and wehrlite, containing 20–35% serpentine, exhibit densities of 2.53–2.77 g/cm³ and compressional velocities of 5.05–5.77 km/s, with porosities to 8.6–9.7%. Unaltered and weakly altered pyroxenites and garnet-pyroxene rocks exhibit 2.98–3.19 g/cm³ and 6.45–7.43 km/s.

Sample	Rock type	Density (g/cm ³)	Porosity (%)	Modal composition (%)	V _p (km/s)	V _s (km/s)
986	Serpentinized lherzolite	2.53	8.6	ol 40, px 30, srp 30	5.05	—
38-16	Garnet-pyroxene rock	2.65	9.7	grt 35, px 20, srp 25, clay 20	5.12	2.80
10-27	Harzburgite	2.76	—	px 55, ol 20, chr-sp 7, srp 18	5.77	3.14
13-79	Serpentinized peridotite	2.77	—	ol 43, px 35, srp 20, ore 2	5.70	3.14
1016	Wehrlite	2.77	—	ol 35, px 20, srp 35, chr-sp 3, ore 8	5.62	2.52
1067	Metamorphosed peridotite	2.86	—	ol 57, grt 20, ore 10, px 6, chr-sp 6	5.72	3.02
23-3	Pyroxenite	2.98	1.97	px 75, amph 25	6.45	3.45

Sample	Rock type	Density (g/cm ³)	Porosity (%)	Modal composition (%)	V _p (km/s)	V _s (km/s)
17-32	Serpentinized peridotite	3.00	0.99	px 50, srp 14, mica 30, ore 6	5.35	3.70
C-1	Pyroxenite	3.01	—	px 95, srp 5	6.89	3.84
38-15	Garnet-pyroxene rock	3.04	1.05	grt 55, pl 20, px 15, srp 10	6.88	3.90
13-43	Pyroxenite	3.11	—	px 100	6.10	3.66
10-71	Pyroxenite, weakly fractured	3.18	—	px 86, ol 10, grt 4	6.70	3.65
38-17	Garnet-pyroxene rock	3.19	—	grt 60, px 20, pl 15, srp 5	7.43	4.18

Table 1. Density, porosity, modal composition and elastic wave velocities of ultramafic rocks of the Lesser Caucasus at pressures to 20 kbar. After [3]. ol — olivine; px — pyroxene; srp — serpentine; grt — garnet; pl — plagioclase; amph — amphibole; chr-sp — chrome spinel; ore — opaque ore minerals.

4.2 Dehydration behaviour

Progressive heating produces an initially smooth increase in compressional-wave travel time, consistent with the ordinary effect of temperature. At higher temperature this is interrupted by an abrupt increase marking the onset of dehydration (Figure 2).

Dehydration proceeds over the interval 500–700 °C, the precise range differing between samples [2]. In apoperidotite serpentinite 29-5 dehydration occurs over 550–700 °C; in apoperidotite serpentinite 28-4 over 600–750 °C. In apodiabase serpentinite 1350 the abrupt change begins earlier, at 400–420 °C.

The difference between samples is governed by the percentage content of serpentine in the rock, by the variety of serpentine present — chrysotile, lizardite or antigorite — by the whole-rock mineral composition, by structural characteristics, and by the pressure, that is to say by the depth at which the process occurs.

Thermal analysis corresponds closely. Pore and fracture moisture evaporates at approximately 100 °C with negligible weight loss; a weak exothermic effect at 250–340 °C is attributed to combustion of minor components; the principal changes occur at 670–680 °C, where an endothermic process with substantial weight loss marks serpentine dehydration and water release. A further exothermic effect appears at 810–820 °C.

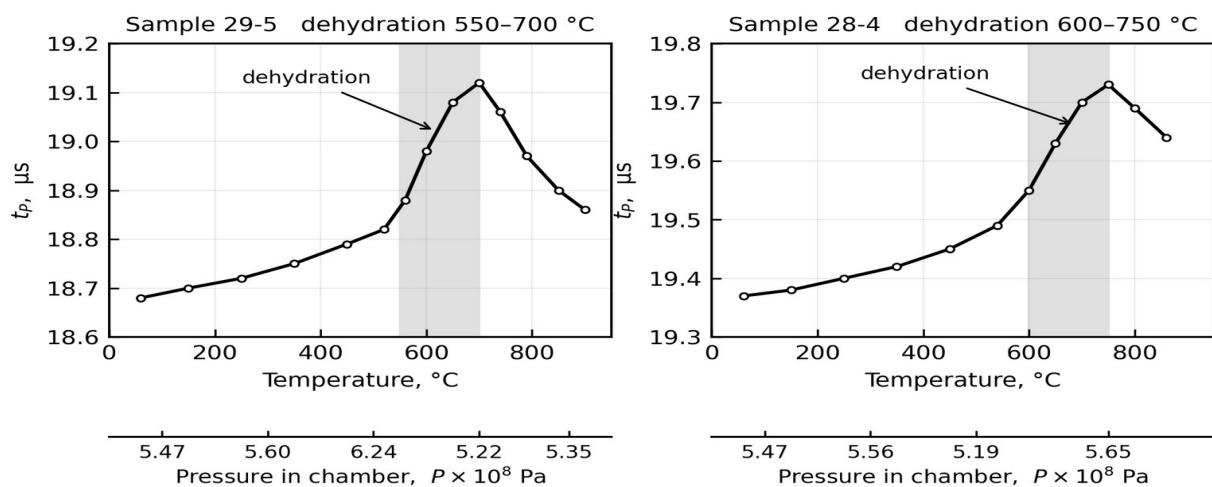


Figure 2. Dependence of compressional-wave travel time on pressure and temperature in apoperidotite serpentinites 29-5 (left) and 28-4 (right). Lower axis gives pressure in units of 10^8 Pa. Redrawn from the published curves of [2]; shaded band marks the 500–700 °C dehydration interval.

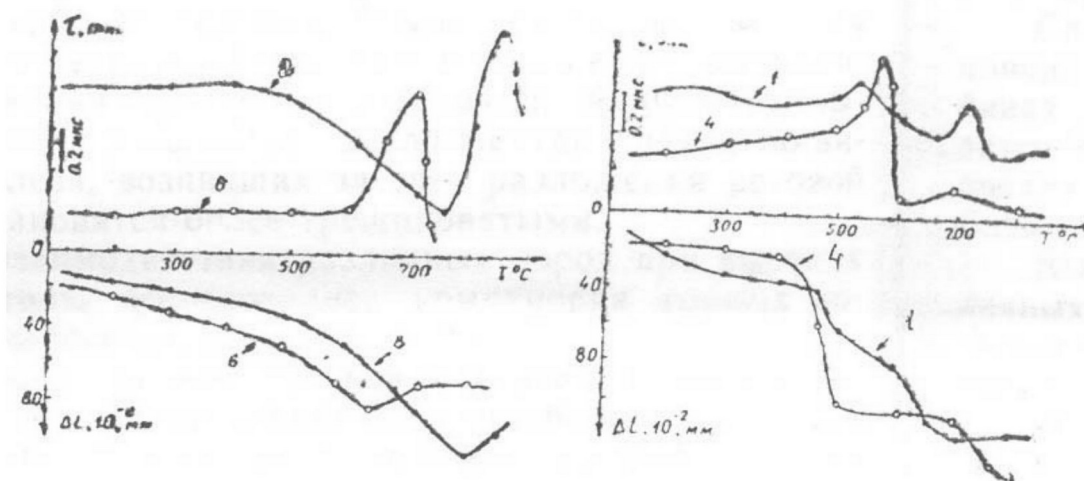


Figure 3. Compressional-wave travel time τ (upper curves) and length change Δl (lower curves) against temperature for rock assemblages at 5 kbar: gabbro-norite with serpentinite, and peridotite with amphibolite. Step-like changes occur over the shaded interval 520–600 °C. Reproduced from the original published figure of [8] at the Author's request, the original providing the more faithful representation.

These assemblages were constructed deliberately, in order to model the arrangement of contrasting layers at depth within the Earth's crust. The wavy character of the curves is attributable to the plastically deformed serpentine present in the samples.

4.3 Volume and density changes

Dehydration is accompanied by step-like volume changes reaching 30% of the volume investigated, registered simultaneously with the velocity changes [2, 8]. Changes of this magnitude, occurring abruptly within a confined volume at depth, were proposed as a possible cause of short-duration processes within the crust, including seismic events.

4.4 Mineralogical transformations

Sample 29-5, apoperidotite serpentinite, consisted before the experiment of chrysotile-lizardite (85–90%) and antigorite (7–10%) in a tangled-fibrous texture, traversed by later veinlets of amorphous ophite frequently accompanied by magnetite. After the experiment it consisted of olivine (forsterite) with traces of enstatite in a microgranular cryptocrystalline aggregate, X-ray confirmed; magnetite, previously dispersed through the mass, was present as veinlets.

Sample 28-4 exhibited a mesh texture with loops outlined by thin magnetite separations and abundant dust-like magnetite within the loops; later veinlets of dense serpentine were contaminated by iron hydroxides. Magnetite content reached 15–20%. After the experiment the sample consisted of forsterite with enstatite, and magnetite content had decreased to 5–10%.

Sample 1350, apodiabase serpentinite, consisted of mesh chrysotile (~55%) and platy antigorite (~25–30%) with brucite developed throughout at approximately 10%, and secondary dust-like magnetite arranged in chains forming thin veinlets. After the experiment it consisted of forsterite with enstatite; the mesh texture was partly preserved, with loops locally filled by magnetite.

In rock assemblages [8], gabbro-norite lost its primary structure through abundant development of an actinolite-tremolite aggregate after pyroxene, with black opaque ore substance separating along that aggregate and numerous fractures filled with ore substance. In quartz diorite, clinopyroxenes altered entirely to amorphous material and opaque ore mineral increased to 3–5% at the expense of clinopyroxene decomposition, with light-yellow rims interpreted as iron hydroxides developing around decomposing hornblende. A peridotite-amphibolite assemblage showed step-like changes over 520–600 °C.

Serpentinized ultramafic rocks and serpentinites of the ophiolite belts of the Lesser Caucasus contain iron and chromium oxides at 5–8%.

4.5 Composition of the released fluid

The apparatus permitted collection of the fluid phase released during dehydration. Gas chromatographic analysis, performed at the Institute of Oceanology, Moscow, determined the presence of alkanes in both fluid samples recovered [4].

Sample	Alkane range determined	Distribution
Fluid sample 1	C ₁₆ – C ₂₁ (low molecular weight)	Maximum at C ₂₀
Fluid sample 2	C ₂₃ – C ₃₅ (high molecular weight)	Dominant fraction; trace quantities of C ₄₅

Table 2. Alkanes determined by gas chromatography in the fluid phase released during dehydration. After [4].

The recovery of alkanes in this carbon-number range is of direct relevance to the question of hydrogen. Alkanes are hydrogen-bearing compounds; their synthesis from carbon-bearing components within the reacting volume necessarily requires a source of hydrogen. The alkane data therefore constitute indirect evidence that hydrogen was generated during dehydration, even though hydrogen itself was not determined.

No direct determination of molecular hydrogen was made. The analysis was directed at hydrocarbon components, hydrogen not being a subject of interest when the work was carried out, and the data reported above represent the complete chromatographic record. No quantitative statement regarding hydrogen yield can therefore be made from these experiments, and none is made here.

5. Discussion

5.1 Serpentinization and deserpentinization: the reaction sequence

Serpentinization proceeds on a global scale in both the modern oceanic crust and the crust of the palaeo-oceans. In the oceanic crust it produces a third, serpentinized layer 4–5 km thick; evidence for this includes protrusions of serpentinized rocks along transform faults and within the mid-ocean ridges. During serpentinization, hydrogen is released as ferrous iron contained within olivine is oxidised to ferric iron. Water acts as the oxidising agent, and hydrogen is liberated from the water as H₂ [1]. The released hydrogen reacts with water to form hydrogen hydrates, which are present throughout much of the oceanic crust.

Deserpentinization is the complementary reaction at depth. At deep crustal levels, under high thermobaric conditions within a confined volume, water is released from the hydrated minerals and reacts with divalent iron, liberating molecular hydrogen. The hydrated mass is transformed into a magmatic focus formed in situ, and reactions between hydrogen and other elements give rise to hydrocarbons, hydrogen sulphide

and further compounds. Part of the hydrogen and of the water, as vapour, remains free. Driven by seismotectonic processes, these components migrate along deep-seated faults into the upper horizons of the crust, where gravitational differentiation leads to the formation of corresponding accumulations.

The same redox couple therefore operates in both reactions. Serpentinization oxidises ferrous iron during hydration at shallow depth and low temperature; deserpentinization releases that water again at greater depth, where it reacts once more with ferrous iron in the residual assemblage. The distinction lies not in the chemistry but in the depth, the temperature, and above all the rate at which fluid is delivered.

The mineralogical record reported in Section 4.4 is consistent with this throughout: the ubiquity of magnetite in the starting materials and its redistribution and recrystallization during the experiments; the presence of iron hydroxides; the increase of opaque ore mineral to 3–5% at the expense of decomposing clinopyroxene; the development of black ore substance along the actinolite-tremolite aggregate in gabbro-norite; and iron and chromium oxides at 5–8% throughout the serpentinized rocks of the belts.

Molecular hydrogen was not measured in these experiments. Its generation is inferred from two independent lines of argument: the mineralogical evidence of iron oxidation reported above, and the recovery of alkanes, whose synthesis requires a hydrogen source within the reacting volume. Direct measurement remains the principal outstanding requirement.

5.1a Products beyond hydrogen and hydrocarbons

The Author has proposed that the conditions generated within the confined volume during dehydration — and in particular the ultra-high pressures that may arise there — bear additionally on the genesis of diamond-bearing structures, mud volcanism and hydrothermal deposits of precious and non-ferrous metals. A detailed examination of these components is the subject of separate consideration and is not developed in the present paper.

5.2 Independent corroboration of the volume change

The volume reduction accompanying dehydration has been examined independently by geomechanical modelling. Garagash [9], modelling a lithospheric section 80 km thick containing an ellipsoidal serpentinite body of semi-axes 200, 100 and 15 km, finds that deserpentinization of the lower crust at 500–600 °C converts serpentinites to secondary olivine and peridotite with release of water, a volume reduction of 10–20%, and an increase in density from 2900 to 3000 kg/m³. The lower crust thins in consequence, producing subsidence of the surface and the formation of negative platform structures.

This modelling postdates the experimental work reported here and cites it. It corroborates independently both the magnitude of the volume change and its geological consequence, by a method — finite-difference continuum mechanics — entirely different from the laboratory measurements. Garagash does not address hydrogen generation.

One difference of interpretation should be noted. Garagash attributes the resulting surface subsidence principally to the upward migration of the released water. In the present author's view the subsidence arises from several contributions acting together: the migration of water, the ascent of magmatic masses, the protrusion of ophiolitic bodies into the upper crust, and the escape of geofluids and gases.

5.3 Relation to the serpentinization model

The process described here is not advanced as an alternative to serpentinization but as a second and deeper stage of the same system. Serpentinization stores water and ferrous iron in hydrous phases at shallow depth and low temperature; dehydration releases them at greater depth and higher temperature, where the same redox couple may operate under conditions favourable to the generation and migration of fluids.

The two differ in a respect that bears directly on the constraint identified by Christiansen and co-authors [1]. Serpentinization is continuous and rate-limited; the hydrogen is generated slowly and in a dispersed state. Dehydration, as the present experiments show, is abrupt: the transition occupies a narrow temperature interval, and the accompanying changes in velocity and volume are step-like rather than gradual. A process of this character releases fluid in quantity over short geological intervals, and is not subject to the same kinetic limitation.

Generation alone, however, does not produce a deposit. Dispersed hydrogen cannot be produced by drilling; a migration pathway and a trap are required. The abrupt character of dehydration, occurring at depth beneath a crust traversed by deep fault systems, supplies the driving mechanism that gradual shallow generation does not.

5.4 Geophysical detectability and field confirmation

The contrast in Table 1 provides the means of identifying prospective bodies. Serpentinized ultramafic rock preserved at depth is characterised by low compressional-wave velocity, low density, high electrical conductivity, elevated magnetization and high plasticity, and appears in seismic sections as a layer of reduced velocity.

This prediction has been tested. A serpentinized layer at 35–50 km beneath Armenia was proposed in 1975 on the basis of laboratory measurements of elastic properties [5], at a time when the interpretation was not widely accepted. Low-velocity layers at the base of the Armenian crust were subsequently identified by the deep seismic surveys of 1973–74, and have been repeatedly detected on deep seismic sounding profiles acquired following the 1988 Spitak earthquake [6, 7, 10].

Laboratory measurement, prediction, and independent geophysical confirmation, over a period of fifty years.

5.5 Associated products

The identification of high- and low-molecular-weight alkanes in the released fluid indicates that hydrocarbon synthesis accompanies dehydration where carbon-bearing components are present. The generation of hydrogen, hydrocarbons and hot aqueous fluids within a single volume, migrating together along deep fault systems into the upper crust, provides a unified account of associations otherwise treated separately.

The present author has proposed that the same process bears on the genesis of diamond-bearing structures, mud volcanism and hydrothermal deposits of precious and non-ferrous metals. Those claims are not developed here and will be treated separately.

6. Availability of apparatus and samples

Approximately ninety per cent of the high-pressure and high-temperature installations used in this programme have been preserved, together with the prepared rock samples from the original experiments.

The author invites collaboration with laboratories elsewhere in the world possessing comparable high-pressure and high-temperature capability. Apparatus, samples and the full experimental record are available to any group wishing to repeat or extend these measurements.

7. Limitations

The principal limitations of this work are stated explicitly.

1. Molecular hydrogen was not measured. The experiments were conducted before natural hydrogen was a subject of interest and no analysis for H₂ was performed. Hydrogen is identified as a predicted product of the reaction on mineralogical and thermodynamic grounds. No quantitative yield is claimed.
2. The oxidation state of iron was not determined. Ferrous and ferric iron contents were not measured before or after the experiments, so the redox pathway is inferred from phase relations rather than demonstrated directly.
3. Raw measurement logs from the original programme have not been preserved. The published tables and curves constitute the surviving record.
4. Instrumentation was that of the 1970s and 1980s. Measurement precision was 5–7%, and uncertainties in temperature determination are not fully documented.
5. The experiments were conducted on a limited sample suite from a single region, and the extrapolation to other orogenic belts containing relics of palaeo-oceanic lithosphere is by analogy.

These limitations define a specific and tractable programme of further work: repetition of the experiments with mass-spectrometric determination of the released gas and with Mössbauer or XANES determination of the ferrous-to-ferric ratio before and after. The original rock samples from the programme are preserved and are available for this purpose.

8. Implications for exploration

The following criteria are proposed for identifying structures prospective for hydrogen and hydrocarbons:

1. Layers of reduced seismic velocity and low density at depth, corresponding to preserved serpentized bodies — the primary target.
2. Layers of reduced velocity at shallower crustal levels, corresponding to potential reservoirs in fractured basement and in sedimentary rocks.
3. Deep fault systems providing migration pathways from the zone of dehydration to the upper crust.
4. Protrusive ophiolite structures along deep faults, indicating serpentized material at depth.
5. Thin high-velocity cover above shallow low-velocity structures, providing seal.
6. Surface volcanism, indicating ascent of magmatic material from foci at depth.

7. Mineralized waters at various crustal depths, and surface geochemical anomalies in hydrogen and hydrocarbons.

A further criterion, concerning the relationship between the character of the migration pathway and the hydrogen content delivered to a reservoir, has been identified by the Author as the subject of a patent application and is therefore withheld from this publication.

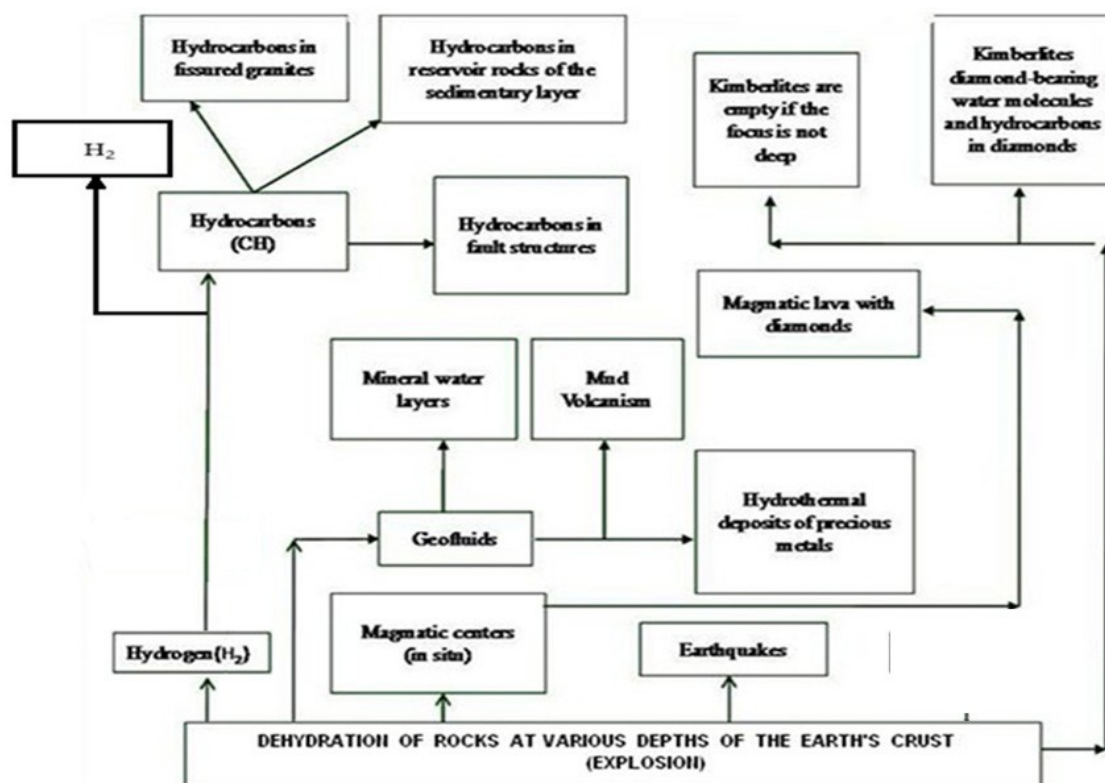


Figure 4. Products generated by dehydration of serpentinized rocks at various crustal depths and their distribution within the upper crust.

9. Conclusions

1. Dehydration of serpentinized ultramafic rocks of the Lesser Caucasus ophiolite belts proceeds over 500–700 °C at crustal pressures, with onset dependent on serpentine variety and fabric, first modelled experimentally in 1987.
2. Dehydration is abrupt, with step-like changes in compressional-wave velocity and volume changes reaching 30% — corroborated independently by geomechanical modelling [9].
3. Hydrous phases break down to forsterite and enstatite, with redistribution of magnetite and development of iron hydroxides. Iron and chromium oxides constitute 5–8% of the serpentinized rocks of the belts.
4. The released fluid contains alkanes C_{16} – C_{21} with a maximum at C_{20} in one sample, and C_{23} – C_{35} with trace C_{45} in the other. Molecular hydrogen was not measured directly; its generation is inferred from the mineralogical evidence of iron oxidation and from the requirement for a hydrogen source in alkane synthesis.
5. The abrupt character of this process distinguishes it from the kinetically limited, continuous generation reported for serpentinization [1], and offers a mechanism capable of supplying fluid in quantity over short geological intervals.

6. Serpentinized rocks measure 2.53–2.77 g/cm³ and 5.05–5.77 km/s against 2.98–3.19 g/cm³ and 6.45–7.43 km/s for unaltered pyroxenites, permitting buried bodies to be identified as low-velocity layers — a prediction made in 1975 and since confirmed by deep seismic sounding.
7. Relics of oceanic lithosphere preserved at depth within continental orogenic belts constitute a class of exploration target distinct from, and deeper than, those indicated by shallow serpentinization models.
8. The circulation may be stated as a whole: oceanic water penetrates the fractured basaltic layer and hydrates the ultramafic rocks of the upper mantle, generating hydrogen; global tectonic processes then carry these hydrated rocks to various depths within the Earth's crust; and where temperatures reach 500 °C, dehydration occurs and hydrogen is generated a second time.

Acknowledgements

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Professor Abovyan died in 2018; the remaining colleagues left Armenia following the closure of the laboratory in 2001, and the author has been unable to contact them since 1998.

The chromatographic analyses were carried out at the Institute of Oceanology, Moscow. The investigations of 1997 were supported by the state budget of the Republic of Armenia under theme 96-340.

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