

EVROPSKÁ UNIE Evropské strukturální a investiční fondy Operační program Výzkum, vývoj a vzdělávání



Geochemistry on the Earth's surface for analytical geochemists

2a.

Geochemistry of the geosphere

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie č. CZ.02.2.69/0.0/0.0/16_018/0002593

Task

- Draw a picture of planet Earth with its internal structure
- Think about how we can know what the interior of the earth looks like...

Topics

- Structure and composition of the solid part of the Earth (= geosphere)
 - Crust
 - Mantle
 - Core
- The origin and development of the planet Earth
- Magmatic processes

Warning : the term geosphere is sometimes used as a general designation for all earth's spheres (hydrosphere, lithosphere, atmosphere...)

GEOCHEMICAL INTRODUCTION

Geochemical nature of the elements

- Most elements show affinity to one group:
- 1. Lithophilic elements form the silicate phase
- 2. Siderophiles form the metallic phase
- 3. Chalcophilic form the sulphide phase
- 4. Atmophilic gaseous elements, volatile
- Some elements have a mixed nature (e.g. O, Fe)
- This division describes the distribution of elements in the Solar System and on Earth





Chemical Fundamentals of Geology and Environmental Geoscience, Third Edition. Robin Gill. © 2015 John Wiley & Sons, Ltd. Published 2015 by John Wiley & Sons, Ltd. Companion Website: www.wiley.com/go/gill/chemicalfundamentals

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Plate 7 Cosmochemical affinities of the naturally occurring chemical elements (cf. Figure 11.4). White squares with grey writing represent elements with no stable or long-lived isotopes (Chapter 10). The terms atmophile, lithophile, chalcophile and siderophile are defined in Chapter 11.

Volatile and refractory elements

Volatile elements

- Low boiling point
- H, He, N₂
- Cd, Pb, S
- Most alkali metals

Refractory elements

- Solid even at high temperatures
- Platinum metals
- Ca, Al, Ti form very refractory oxides and silicates

Two extremes, the remaining elements form a gradual transition



Převzato z McSween & Huss (2010)

A cosmochemical periodic table, illustrating the behavior of elements in chondritic meteorites. Cosmic abundances are indicated by symbol sizes. Volatilities of elements reflect the temperatures at which 50% of each element would condense into a solid phase from a gas of solar composition. As in Figure 1.2, the chemical affinities of each element, lithophile for silicates and oxides, siderophile for metals, and chalcophile for sulfides, are indicated. Some of the most highly volatile phases may have remained uncondensed in the nebula. Stable, radioactive, and radiogenic isotopes used in cosmochemistry are indicated by bold outlines, as in Figure 1.2. Abundances and 50% condensation temperatures from tabulations by Lodders and Fegley (1998).



Figure 11.5 Element fractionation in the Earth (white bars) and the Moon (grey bars). The length of the bars indicates the approximate degree of depletion (left) or enrichment (right) of each 'volatility group' of elements relative to Solar-System average abundances – see **logarithmic** scale at top. The arrow on the right indicates the predicted order of condensation as the solar nebula cooled. Because Si is the reference element for expressing both terrestrial/lunar and Solar-System abundances (Figure 11.2), the Si group of elements registers neither enrichment nor depletion in this diagram.

Chemical Fundamentals of Geology and Environmental Geoscience, Third Edition. Robin Gill. © 2015 John Wiley & Sons, Ltd. Published 2015 by John Wiley & Sons, Ltd. Companion Website: www.wiley.com/go/gill/chemicalfundamentals

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STRUCTURE OF THE EARTH

Structure of the Earth



Rust Country adapted from the original : By Kelvinsong - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=23966175

Sources of knowledge of the Earth's interior

- Abrupt breaks in seismic wave velocity
- Differentiation of meteorite parent bodies

 captured in a varied spectrum of possible compositions
- Mineralogical and petrological properties of rock samples raised to the surface by magmatic processes
 - Reconstruction of pressure-temperature (P-T) conditions

Seismic waves

- Pressure (P) and shear (S) waves
- The influence of density and compactness of the environment (or elasticity)² on the speed of wave propagation
- Earth's density in the range of 2.8 to 12 g/cm³
 - Effect of compositional change and recrystallization on more compact minerals with depth



Public domain (USGS)

Seismic waves



Discontinuities

- 1. Base of the crust (Mohorovičić disc., Moho) ^(a)
 - 40 km below the continents
 - 5-7 km under the oceans
- 2. The base of the lithosphere
 - 80 km under the oceans
 - A gradual transition
 - The lower edge of solid lithospheric plates
 - Below it is the asthenosphere
- 3. Transition of olivine structure to spinel structure (410 km)
- 4. Base of the upper mantle (660 km)
 - Transition of all minerals to perovskite and additional magnesio-wüstite (Fe-Mg oxide)
- 5. D" (mantle/core interface, 2900 km)
- 6. Inner/Outer Core Interface (5150 km)
 - Fe and Ni in metallic form
 - The movement of the outer fluid core creates the Earth's magnetic field



0

Crust

- Only 0.7% of Earth's mass
- Dominantly from silicates
- 99% made up of 8 elements (O, Si, Al, Fe, Ca, Mg, Na, K)

- A. Oceanic crust
- B. Continental crust

Plate tectonics

Adapted from USGS image (Public Domain)



The processes of plate tectonics change the chemical composition of individual parts of the Earth.

Oceanic crust

- 70% of the surface
- Average thickness 7 km (least on mid-ocean ridges ~4 km, most on oceanic volcanic plateaus over 10 km)
- **Young** <200 Ma
- Relatively homogeneous
- Higher density basalts (enriched in Ca, Mg and Fe)

Continental crust

- Topographically higher, thicker average of 40 km (20-80 km)
- Older oldest parts > 3.8 Ga
- Varied lithology averageable to "andesitic composition"
- Enrichment by Si, Na, K, volatile substances and radioactive elements
- Enriched with incompatible elements
 - cont. crust contains approx. 50% of the original contents of the primary mantle
- The existence of a developed continental crust is a unique feature of Earth compared to other rocky planets



Public domain (USGS)

Mantle

- Represents 83% of the volume and 68.3% of the mass of the Earth
- Compared to the crust, it is enriched in Mg, contains less Fe and Si, and is depleted in volatile and radioactive elements
- On the basis of seismics divided into
 - 1. Upper mantle
 - 2. Transition zone
 - 3. Lower mantle

Upper coat

- Begins at the Moho gradual transition rather than a sharp boundary
 - Uncertainty in the position of the crust/mantle divide
- Includes the lower part of the lithosphere
 - The solid outer layer of the Earth
 - Brittle deformations (rigid material)
- Beneath the lithosphere lies the **asthenosphere**
 - Elastic deformation (elastic material)
 - Low wave speed zone possible presence of melt
 - Zone of convective movements

Mantle composition

- Estimates based on
 - P-wave speed,
 - composition of ophiolite complexes and xenoliths from basalts and kimberlites and
 - conditions of formation of basaltic magma
- We assume a composition of ultramafic rocks – peridotite (ol.+px.) and eclogite (gr.+px.)
- Different composition under oceanic and continental crust
- Peridotite under Moho depleted of incompatible elements during magma formation
- Primitive peridotite called pyrolite (pyroxene-olivine)



Adapted from Misra (202

Mantle composition

- Overall chemical composition very similar across the mantle
- Mineralogical composition is a function of depth (i.e. pressure)
- In the transition zone, olivine changes to a spinel structure (ringwoodite)
- From approx. 300 km px. forms solid solution with gr.
- In the lower mantle, a mineral mixture of Mg-perovskite (MgSiO₃), Ca-perovskite (CaSiO₃) and magnesiowüstite (MgFeO)



Core

- It makes up 16% of the volume and 31% of the mass of the Earth
- Earth's average density is 5.515 g/cm³ the highest of any planet, with the crust and mantle being less dense on average
 - The heavy core assumption
- A lower content of siderophilic elements in the mantle and crust than in chondrites
 - We assume they are in the core
- An alloy of Fe, Ni (4-5%) and Co (0.2%), smaller amounts of S, C, O and Si.
 - Other estimates indicate higher contents of O (5%) and S (2.7%), possibly also Si (up to 7.3%)
- Due to the low viscosity and impermeability to S waves, we assume that the outer core is molten
- The inner core is solid and the crystals have a remarkably uniform orientation
- The source of Earth's magnetic field



The internal structure of the Earth determined by the propagation of seismic waves from earthquakes. Essential minerals of the mantle are garnet (gr), magnesio-wüstite (mw), olivine (ol), perovskite (pv), pyroxene (pyr), and ringwoodite (rg).

The overall composition of the Earth

- The ratios of elements and isotopes in Earth roughly correspond to chondritic meteorites
- The average composition of Earth will be similar to the average composition of chondrites
- Conversion to individual parts of the Earth based on density and elastic properties – different approaches, e.g.:
 - The core corresponds to the diameter of FeNi in chondrites
 - The silicate part of the Earth (*bulk silicate earth = BSE*) representing mantle and crust corresponds to silicates in chondrites
 - Problem: which meteorite should be used as default? How should the average be weighted?
 - Other studies demonstrate that the composition of contemporary meteorites does not correspond to the Earth and the material that dominantly formed it.
- Therefore, estimating the composition of the Earth from meteorites is problematic without knowledge of a meteorite that clearly represents the original material

The overall composition of the Earth

- The second approach is to combine the average composition of differentiated parts of the Earth
 - We know the atmosphere, the hydrosphere and the crust
 - The composition of the mantle and core depends on the used model
- The data presented correspond to a combinationbased procedure
 - 1. BSE estimation based on the composition of basalts, ophiolites, komatiites and xenoliths, including the effects of core formation, etc.
 - 2. Volatility trend (the process of condensation of elements from the nebular disk)

Ζ	Element	Abundance	Ζ	Element	Abundance	Ζ	Element	Abundance
1	н	36.9?	32	Ge	10.2	63	Eu	0.1035
2	He		33	As	1.73	64	Gd	0.363
3	Li	1.69	34	Se	3.16	65	Tb	0.0671
4	Be	0.052	35	Br	0.13	66	Dy	0.448
5	В	0.292	36	Kr	?	67	Но	0.1027
6	С	44?	37	Rb	0.76	68	Er	0.294
7	N	0.59	38	Sr	14.4	69	Tm	0.0447
8	0	316700	39	Υ	2.88	70	Yb	0.300
9	F	15.8	40	Zr	7.74	71	Lu	0.0449
10	Ne	?	41	Nb	0.517	72	Hf	0.203
11	Na	2450	42	Мо	1.71	73	Та	0.0281
12	Mg	148600	43	Тс		74	W	0.171
13	Al	14330	44	Ru	1.71	75	Re	0.0674
14	Si	145900	45	Rh	0.227	76	Os	0.898
15	Р	1180	46	Pd	0.831	77	Ir	0.889
16	S	8930	47	Ag	0.099	78	Pt	1.77
17	Cl	264	48	Cď	0.068	79	Au	0.157
18	Ar	?	49	In	0.0049	80	Hg	0.0065
19	К	225	50	Sn	0.34	81	TI	0.0073
20	Ca	16570	51	Sb	0.061	82	Pb#	0.172
21	Sc	11.1	52	Те	0.39	83	Bi	0.0057
22	Ті	797	53	1	0.036	84	Po	
23	V	104	54	Xe	?	85	At	
24	Cr	3423	55	Cs	0.055	86	Rn	
25	Mn	2046	56	Ba	4.33	87	Fr	
26	Fe	320400	57	La	0.434	88	Ra	
27	Co	779	58	Ce	1.114	89	Ac	
28	Ni	17200	59	Pr	0.165	90	Th	0.0543
29	Cu	82.7	60	Nd	0.836	91	Pa	0.05 15
30	Zn	47.3	61	Pm		92	U	0.0152
31	Ga	4.42	62	Sm	0.272		Sum	100.02
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# Nonradiogo Source of dat	enic Pb only. ta: Kargel and Lewis									



undance of elements in the Earth's upper crust . Not shown : Noble Gases, Tc (43), Pm (61), and all elements after Bi (83), except for Th (90) & U(92), B. Haxel , Sara Boore , and Susan Mayfield from USGS, vectorized by User:michbich - http://pubs.usgs.gov/ fs /2002/fs087-02/, Public Domain ,

Composition of the Earth



atmů/10⁶ atomů Si
Composition of the Earth - comparison

	Earth	Crust	Crust	Crust
Element	Mass %	Mass %	Atomic %	Volume %
0	30	46	61	90.95
Si	15	28	20	0.84
AI	1.1	8	6.2	0.46
Fe	35	6	1.9	0.5
Mg	13	4	1.4	0.38
Са	1.1	2.4	1.9	1.44
К	-	2.3	1.8	1.19
Na	-	2.1	2.5	1.08
Other	-	< 1	-	_
S	1.9	-	-	_
Ni	2.4		-	_
In total	99.5	98.8	96.8	96.84



GENESIS AND DIFFERENTIATION OF THE GEOSPHERE

The formation of the Earth



Planetary accretion

- The protoplanetary disk cools
- Condensation
- Composition of forming bodies determined by the distance from the Sun
 - Refractory substances (rock planets)
 - Volatiles (gas and ice giants)
- The main phase of planet formation took place during the first 30 Ma



The formation of the Earth

- Formed shortly after formation of the Solar System
 - Comparison of W isotopes in the mantle and meteorites

The formation of the moon

- Giant impact theory
 - Earth's edge-on collision with a Mars-sized body (Theia)
 - Chondritic composition
 - The Earth has about 90% of its final mass before the collision
 - Both bodies differentiated into a metal core and a silicate mantle
- Age based on isotopes 4.48 ± 0.02 Ga



Public domain (NASA)

The formation of the moon



- The Moon is formed from the mantle material of an impactor ejected into space around the Earth
- Formed in 10-100 years
- A metal-depleted moon
 - 8-12% Fe compared to 31% on Earth
 - Theias metal core incorporated into Earth (10% mass)

Geochemistry of the Moon

- The isotopic composition of oxygen corresponds to that of the Earth
 - Originating at the same distance from the Sun?Blending on impact?
- The energy released by the collision would melt the released material
 - The moon is formed as a molten body a magmatic ocean
 - The origin of a magmatic ocean on Earth too?

Accretion models

- Models of the formation and division of the Earth into mantle and core
- Two basic views
 - 1. Homogeneous
 - 2. Heterogeneous
- Both models assume formation from meteoric material from the asteroid belt
- The difference lies in the mechanism of division into silicates and metals

Homogeneous accretion

Adapted from Misra (2012

- Condensation of material from the protoplanetary disc was completed before accretion began
- The composition of the resulting material is a function of distance from the Sun – the further away, the more volatile the material, the excess gas carried away
- The earth was then created by accretion as a cold, homogeneous and undifferentiated mixture of silicates and metals
- Subsequent melting (meteor bombardment, gravitational compression, radioactive decay)
- The molten material has split into the core and the mantle – the heavier material sinks to the bottom, the lighter remains on top



Homogeneous accretion

- The model explains the density distribution well
- Problems
 - It is unlikely that a planet the size of Earth would attract condensates corresponding to only one temperature
 - Venus, Earth and Mars shouldn't have atmosphere – no volatiles would be present at the appropriate condensation temperature

Heterogeneous accretion

- The gradual growth of the planet by simultaneous accretion and condensation of material as the original nebula cools
- The result is a stratified planet:
 - The most refractory material is in the middle (Fe+Ni) because it condensed first
 - The less refractory silicates follow
 - Finally, the atmosphere (and hydrosphere) from volatile phases
- The model does a good job of explaining the expanding material source zone as the planet grows



- A widely accepted theory, but problems arise
 - The contents of siderophilic elements in the mantle do not correspond to expectations
 - The zonality of a planet cannot be estimated from condensation temperatures

Adapted from Misra (2012

Magmatic ocean

- We assume that the Earth was melted on a large scale at least once
- Melting homogenized the composition created by heterogeneous accretion

 most features were not preserved
- Drops of molten metal, sink to the bottom where they form larger formations and descend through the solid mantle into the core



Primitive cloak

Table 11.3. Primitive Mantle Concentrations

CONCENTRATIONS							
Li	1.6	Ge	1.1	Nd	1.225		
Be	0.066	As	0.13	Sm	0.381		
В	0.5	Se	0.05	Eu	0.145		
С	250	Br	0.075	Gd	0.526		
F	26	Rb	0.60	Tb	0.093		
Na	2545	Sr	19.9	Dy	0.651		
Mg	219407	Y	4.05	Ho	0.146		
A1	22985	Zr	10.5	Er	0.428		
Si	214766	Nb	0.651	Tm	0.058		
Р	95	Мо	0.065	Yb	0.439		
S	350	Ru	0.0042	Lu	0.065		
C1	330	Rh	0.001	Ηf	0.283		
Κ	240	Pd	0.005	Ta	0.037		
Ca	23858	Ag	0.008	W	0.021		
Sc	15.5	Cd	0.04	Re	0.00028		
Ti	1153	In	0.013	Os	0.0034		
V	82	Sn	0.175	Ir	0.0033		
Cr	2935	Sb	0.005	Pt	0.0068		
Min	1080	Te	0.013	Au	0.00075		
Fe	65500	Ι	0.011	Hg	0.01		
Co	105	Cs	0.021	T1	0.007		
Ni	1890	Вa	6.189	Pb	0.18		
Cu	30	La	0.624	Вi	0.0025		
Zn	56	Ce	1.637	Th	0.0813		
Ga	3.9	Pr	0.238	U	0.0203		

All concentrations in ppm.

• The composition corresponds to BSE

Earth at the beginning of the Archean



- Thick basaltic crust
- Ocean
- Small extent of land (domestic granitoids)
- Atmosphere with CO₂
- Sun 25% brightness
- 1 day = 10 hours

Formation and development of the crust

- From a comparison with other planets, we assume a basaltic primordial crust similar to the current oceanic crust
- No leftovers available
- Probably formed soon after accretion
- Warmer upper mantle faster cycle of formation and destruction
 - The question of plate tectonics is not clarified
 - The oldest preserved oceanic crust ca. 1 Ga
 - Xenoliths indicator of some form of rock circulation

Early continental crust

- Oldest continental crust from partial melting of primitive mantle
- The oldest preserved crust 3.8-4.0 Ga
- The oldest minerals 4.4 Ga old zircons , probably from granitoid rocks
 - The O isotopes within indicate the existence of oceans



Zircon from the Jack Hills region of Western Australia - <u>the oldest</u> known mineral on Earth.

Bark composition and growth Adapted from Misra (2012) Primitive mantle-normalized ratios 100 HADEAN ARCHEAN PROTEROZOIC O Continental Reducing atmosphere Oxic atmosphere Oceanic crust High T / Low P Modern island Subduction regime Arc regime 10 Higher⁸⁷Sr/86S Intense Eu depletion meteoric 100 bombardment melting 80

The composition of the oceanic and continental crust relative to the composition of the primitive mantle shows a surprisingly complementary evolution, where the continental crust is significantly enriched with incompatible elements.

La Ce

Sr P

Bb Ba

Th

Ta Nb

Hf

Zr Eu Ti Yh



And a little about volcanism

FORMATION AND EVOLUTION OF MAGMA

Formation of magma



Adapted from Misra (2012)

- The basic environment of magma formation from the point of view of plate tectonics
 - 1. Constructive board edges
 - 2. Destructive board edges
 - 3. Oceanic intraplate environment
 - 4. Continental intraplate environment

Causes of melting

- The mantle is made up of solid rock only approx. 1% in the asthenosphere is melt
- The main source of melt is decompression melting and the drop in temperature of the solidus (melting point of the rock) due to the presence of volatile substances
- Beneath oceanic rifts, melt is produced by a drop in pressure on upwelling peridotite

- Similarly, intraplate magmatism

 In subduction zones, the descending plate is heated, water is released from hydrated minerals and partial melting is initiated by the resulting fluids

Hot spots



Figure 11.32. Map showing the distribution of mantle plumes (triangles), P-wave velocity anomalies (m/sec) averaged over the whole lower mantle (red lines), and location of the DUPAL and SOPITA isotope anomalies (pale red regions). Mantle plumes are located in regions of slow lower mantle seismic velocities, implying high temperatures. The DUPAL and SOPITA anomalies are located near seismic velocity minima. After Castillo (1989).

Partial melting

- Formation of basaltic magma by melting of the upper mantle (olivine composition)
- Olivine is heated and reaches the temperature on the solidus curve (c1)
- A melt with a composition of m₁ is formed; with a further increase in temperature, olivine continues to melt and amount of molten forsterite increases the melt moves to m₂, the remaining crystals have a composition of c₂
- The complete transition to the melt occurs at a temperature over 1800 °C (m₃)
- The gap between the onset of melting and complete melting is crucial for magma genesis
- Simple melting occurs only for end members that do not behave like solid solutions



Partial melting

- The result is a magma (m₂) poorer in Mg than the source rock (c₁) and a refractory residue richer in Mg (c₂)
- What does the composition of the resulting phases depend on?



Adapted from Gill (201

Partial melting

- Mixtures of minerals melt earlier than individual minerals
- All minerals from the beginning of melting contribute to the composition of the resulting melt (magma)
- Minerals don't melt one by one!

Decompression melting



- Mid-ocean ridges
- The material in the solid mantle performs convective movement under the influence of temperature and the related density difference
- Movement to the surface will cause a drop in pressure on the rock and a transition across the solidus curve (X–Y line)
- There is no need to supply heat for melting – on the contrary, the emerging material is cooled by the expansion work performed
- Intraplate volcanism
- Combined effect of warmer material transport and decompression

Primary magma

- Melting of the mantle produces basaltic primary magma
- Processes of differentiation and mixing give rise to other advanced types of magma
- Properties determined by origin, intensity and mechanism of partial melting

Dependent on tectonic position

• The variety of igneous rocks is related to the origin and differentiation of the magma

Trace elements in magma . processes

- An important source of information on additional processes
- E.g. rare earth elements
- Fractionation into melt/crystals
- Equilibrium fractionation
- Rayleigh fractionation



Lava

- Rock melt on the Earth's surface
- Forms parts of volcanoes, lava flows, etc.
- The way lava flows and thus the geometry of lava formations depends on viscosity Arenal Volcano (Costa Rica)





Melt viscosity

- It increases with the degree of polymerization of silicates
 - Acidic melts (rhyolites) more viscous

- Basic melts (basalts) - less viscous

- Shorter polymers "flow better"
- Viscosity is drastically reduced by the presence of water $O-Si-O-Si-O-Si-O-H + H_2O \rightarrow O-Si-O-Si-OH + HO-Si-O-H$

Shorter polymer

Shorter polymer

Long polymer

Volatile components

- The role of other volatile components is also crucial for viscosity
- H₂O, CO₂, H₂, HCl, N₂, HF, F₂, Cl₂, SO₂, H₂S, CO, O₂, NH₃, S₂, He, Ar
- Critical point –> supercritical fluid
 - At depths below 1 km, the difference between the liquid and gaseous state disappears
 - water: 21.8 MPa, 371 $^{\circ}$ C
 - CO₂: 7.3 MPa, 31 °C
- Fluid pressure



Solubility of volatile components in silicate melts

- Melt with dissolved volatiles = melt + volatiles $V_{t+f} < V_t + V_f$
- A large amount of volatile substances are stable in the melt only at high pressures

Separation of volatile substances from the melt

- Pressure drops with upward movement.
- The stability of dissolved volatile components decreases.
- Unsaturated magma -> saturated magma -> supersaturated magma.
- The excess is separated into a fluid phase – exsolution, boil
- Crystallization of anhydrous minerals under constant p –> fluid supersaturation & retrograde, secondary boiling; it can also occur when the temperature drops!



Eruption

- The leakage of volatile substances will also cause an increase in viscosity
 - Polymerization
 - Presence of bubbles
- Highly viscose magma leads to explosive eruptions

Pahoehoe (Hawaii)



Summary

- The Earth's interior is made up of concentric shells differing in density and composition: core (liquid outer and solid inner), mantle and crust (continental and oceanic)
- Differentiation into primitive shell (BSE bulk silicate Earth) and metallic core is best explained by magmatic processes under high PT conditions in a magmatic ocean
- The oldest oceanic crust is 200 Ma old, the primary crust was basaltic and was recycled by the same processes that affect oceanic crust today
- The oldest continental crust is 4.4 Ga old and was formed by partial melting of the primitive mantle, growing episodically by gradual accumulation
- Primary magma is formed in the upper mantle by partial melting of mantle rocks, especially by decompression melting



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