November 2009

GEO1-1112 Chemistry of the Earth I

EINDTOETS 2009

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Name _____

Student nummer _____

SECTION A: MULTIPLE CHOICE: ANSWER ALL 14 QUESTIONS SECTION B: LONG QUESTIONS: ANSWER 2 OUT OF 5 QUESTIONS

NOTE: Physical constants and a periodic table are given at end of this exam paper

A. MULTIPLE CHOICE QUESTIONS

Answer all questions by placing a cross in the box against the correct answer

A1. Which of the following elements would you predict to be most mobile in an aqueous fluid above a subducting slab in a subduction zone?

A	Κ
B	Ca
C	Si
\square D	Fe

A2. Which of the following analytical techniques would you use to measure δ^{18} O in a rainwater sample?



Inductively coupled plasma atomic emission spectrometry (ICP-AES)

- B Inductively coupled plasma mass spectrometry (ICP-MS)C Gas Source mass spectrometry (GS-MS)
- C Uas Source mass spectrometry (US-MS)
- Electron microprobe microanalysis (EMPA)

A3. How many valence p electrons are there in the O²⁻ anion?

A	0
B	2
C C	4
D	6

A4. Which of the following elements would you predict to have the lowest first ionization energy?

A	Na
B	Cl
C	Fe
D	Κ

A5. Why do geochemists typically normalize trace element concentrations to *chondrite*?

A	Because some elements were anomalously unstable during nucleosynthesis (e.g. B, Be)
B	Because some elements were anomalously stable during nucleosynthesis (e.g. Fe)
□ C	Odd atomic number elements are more abundant than those with an even atomic number
🗌 D	Even atomic number elements are more abundant than those with an odd atomic number

A6. Three nuclides, ${}^{12}B$, ${}^{12}C$ and ${}^{12}N$ all have the same mass. Which of the following terms can be used to describe their relationship to one another?

A	Isotopes
B	Isobars
C C	Isomers
D	Isotones

A7. Which of the following groups of elements fall into the Chalcophile group as defined by Goldschmidt?

□ A	As, Sb, Se
B	Ni, Co, Ge
C	Na, K, Mg
D	Ar, N, O

A8. Which of the following rock types was suggested by Taylor & McLennan (1985) as an approximation for average continental crust?

□ A	Andesite
B	Basalt
□ C	Granite
D	Sandstone

A9. What is the average distance and of the electron from the nucleus in a helium ion (He⁺) for the 2*p* orbital. $a_0=0.529$ Å

A	1.3 Å
B	1.6 Å
C	2.6 Å
D	3.2 Å

A10. What is the ground state electron configuration for the element Iron (Fe), atomic number 26

	[Ar] 3d ⁸
B	$[Ar] 4s^2 4d^6$
C	$[Ar] 4s^2 3d^6$
D	$[Ar] 4d^8$

A11. Which of the following parameters does NOT influence δ^{18} O fractionation in water vapour in clouds?

A	Latitude
B	Temperature
C	Atmospheric pressure
D	Amount of rainfall

A12. What is the co-ordination number (number of bonds with adjacent atoms) of oxygen in solid ice?

A	2
B	4
C C	6
D	8

A13. In the solution to the Schrödinger equation what value is given to the angular momentum quantum number for a *d* orbital?

A	0
B	1
C	2
D	3

A14. What is the current minimum age for the Earth, measured using U-Pb isotopes in zircons

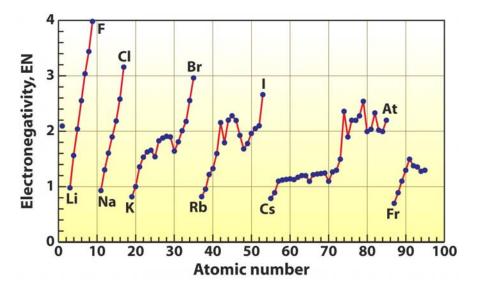
A	3.5 Ga
B	4.03 Ga
C	4.4 Ga
D	4.56 Ga

PART B: ANSWER 2 OUT OF THE FOLLOWING 5 QUESTIONS

OPTION B1: Atomic structure and the Periodic Table

The modern periodic table explains the variation in many chemical properties of the elements from both a theoretical (quantum mechanical) and practical basis. Relative electronegativities can be both measured and predicted from the periodic table with excellent agreement.

- (a) What is the definition of **electronegativity?** [4 Marks]
- (b) The figure below shows how electronegativity varies with atomic number for the first 96 elements in the periodic table.



Why does electronegativity increase on going across the second period elements from Li to F? Give as much detail as you can about changes in forces and distances within the atom.

[6 Marks]

(c) Explain in as much detail as you can why the slope of the plot is not linear between K and Br

[6 Marks]

(d) Why is electronegativity a more useful property than ionization energy or electron affinity for explaining the properties of liquids such as water or ethanol?

[4 Marks]

OPTION B2: Elemental abundance in the universe

The figure below shows the ratio between element concentrations in the bulk silicate Earth and those in C1 carbonaceous chondrites (which are assumed to represent the bulk composition of the whole Earth)

> Bulk Silicate Earth / CI chondrite (Mg basis) 100 10 REE Hf Tł Abundance 0.1 0.01 Os Ir 0.001 0.0001 Element

(a) Explain which two processes cause many of the elements to have lower concentrations in the bulk silicate Earth than C1 carbonaceous chondrites (i.e. why is the ratio much less than 1?).

[4 Marks]

(b) Why is it assumed that C1 carbonaceous chondrites have a similar composition to the bulk solar system? What other evidence is available to show this.

[4 Marks]

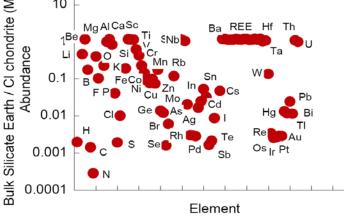
(c) What process or processes were responsible for producing the general decrease in abundance with increasing atomic number as the elements were formed in the cosmos? Briefly describe each of the important steps that took place in the big bang.

[6 Marks]

(d) Why are some elements anomalously high or low in abundance when compared with the trend you just described? (give as much detail in your answer as you can, with information about the chemical or physical processes that are important)

[6 Marks]

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OPTION B3: Properties of Water

Ocean currents are controlled by the relative temperature and salinity of water as it circulates across the Earth's surface

(a) Explain the trend in the boiling points *vs*. mass for the following hydrides of the group VI elements. Describe the role of intermolecular forces in your answer.

HF	292.7 K
HCl	189.5 K
HBr	206.8 K
HI	237.8 K

[4 Marks]

(b) Describe as clearly as you can one of the most important molecular processes that causes water to sink to the bottom of the ocean in high latitude regions. Illustrate your answer with diagrams as necessary.

[8 Marks]

(c) Water can travel great distances at depth in the oceans before it rises to the surface once more. Which property of water leads to this observation?

[2 Marks]

(d) Explain why, at a temperature of above 374 ^{o}C , Na $^{+}_{(aq)}$ and Cl $^{-}_{(aq)}$ will immediately precipitate to form NaCl $_{(s)}$

[6 Marks]

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OPTION B4: The age of the Earth

(a) ²³⁸U has a half life of 4.5 Ga and ²³⁵U a half life of 0.7 Ga. Assuming that the two isotopes were to be found in a proportion of 1:1 at the time of formation of the Earth, use radioactive decay equations to calculate an age for the Earth. Assume the modern ²³⁵U/²³⁸U ratio to be 0.007.

[8 Marks]

(b) What methods are available for determining the age of the Earth? In your answer give details about the types of rocks or minerals that could be investigated and the analytical methods that could be applied.

[6 Marks]

(c) What information is provided about the formation of the Earth from very short-lived radiogenic isotopes (e.g. ²⁶Al). In your answer give an example of a major process, early in the Earth's history that could be dated.

[6 Marks]

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OPTION B5: Analytical Techniques in Geochemistry

(a) What is the difference between a *major element* and a *trace element* in geochemistry? In your answer give the definitions of a major and a trace element with as much detail as you can.

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[4 Marks]

- (b) Both the x-ray fluorescence spectrometer (XRF) and the electron microprobe (EMPA) use xrays to determine the composition of a geological sample. Explain how both of these techniques can be used and work. In your answer give the following details
 - the primary beam of energy used to excite the sample
 - the secondary beam that is measured
 - what happens in the sample to create the secondary beam (describe only once as it's the same for both techniques)
 - what kind of sample can be measured and on what scale
 - what is measured: major elements, trace elements or isotopes

[8 Marks]

- (c) A contamination problem has been discovered in Utrecht's city sewage works that originates from De Uithof. Data is required to support a court case against the Department of Earth Sciences. It is your task to compare potential pollution sources from the following labs against the sewage effluent. The sewage samples that have already been measured contain a lot of soluble cations including sodium (Na), potassium (K), iron (Fe), rare earth elements (REE), lead (Pb) and uranium (U).
- i. rock digestion lab: typical samples include basalt, granite
- ii. marine geochemistry lab: the lab measures only seawater samples
- iii. environmental soil science lab: many canal sludge samples from an industrial area west of Utrecht were recently measured
 - Describe an analytical technique, or more than one technique if you think it is necessary, that you could use to measure sewage water samples
 - Is high accuracy and/or precision required to distinguish between the different lab effluents?
 - Which of the three labs is most likely responsible for the contamination problem?

[8 Marks]

Physical Constants

Avogadro's number	$N_A = 6.022 \text{ x } 10^{23} \text{ atoms mol}^{-1}$
Bohr radius	$a_0 = 0.529 \text{ Å} = 5.29 \text{ x } 10^{-11} \text{ m}$
Charge on an electron	$e = 1.602 \times 10^{-19} C$
Mass of an electron	$m_e = 9.109 \text{ x } 10^{-31} \text{ kg}$
Permittivity of a vacuum	$\varepsilon_0 = 8.854 \text{ x } 10^{-12} \text{ C}^2 \text{J}^{-1} \text{m}^{-1}$
Planck's constant	$h = 6.62 \times 10^{-34} \text{ Js}^{-1}$
Speed of Light in a vacuum	$c=2.998 \text{ x } 10^8 \text{ ms}^{-1}$
Universal gas constant	$R = 8.314 \text{ Jmol}^{-1} \text{K}^{-1}$

Equations

$$F(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2} \qquad r_n = \frac{\varepsilon_0 n^2 h^2}{\pi Z e^2 m_e} = \frac{n^2}{Z} a_0 \qquad v = (3.29 \times 10^{15} \, \text{s}^{-1}) Z^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$
$$V(r) = \frac{q_1 q_2}{4\pi\varepsilon_0 r} \qquad r = \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right\}$$
$$E_n = \frac{-Z^2 e^4 m_e}{8\varepsilon_0^2 n^2 h^2} = -(2.18 \times 10^{-18} \, J) \frac{Z^2}{n^2}$$

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Hydrogen 1.008																	4.003
Н																	Не
- 11																	ПС
Lithium	Beryllium											Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
6.941	9.012											10.811	12.011	14.007	15.999	18.998	20.180
Li	Be											В	С	N	0	F	Ne
Sodium 22.990	Magnesium 24.305											Aluminum 26.982	Silicon 28.086	Phosphorus 30.974	Sulfur 32.066	Chlorine 35.453	A rgo n 39.948
Na	Mg											AI	Si	Р	S	CI	Ar
Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine	Krypton
39.098	40.08	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
K	Са	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	Technetium	Ruthenium	Rhodium	Palladium	Silver	Cadmium	Indium	Tin	Antimony	Tellurium	lodine	Xenon
85.47	87.62	88.906	91.224	92.906	95.94	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.75	127.60	126.90	131.29
Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	I	Xe
Cesium	Barium	Lanthanum	Hafnium	Tantalum	Tungsten	Rhenium	Osmium	Iridium	Platinum	Gold	Mercury	Thallium	Lead	Bismuth	Polonium	Astatine	Radon
132.90	137.33	138.91	178.49	180.95	183.85	186.21	190.2	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
Cs	Ва	La	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Ро	At	Rn
Francium	Radium	Actinium	Dubnium	Joliotium	Rutherfordium	Bohrium	Hahnium	Meitnerium	Ununnilium	Unununium	Ununbium	Ununtrium	Ununguadium	Ununpentium	Ununhexium	Ununseptium	Ununoctium
(223)	(226)	(227)	(261)	(262)	(263)	(262)	(265)	(266)	(272)								
Fr	Ra	Ac	Db	JI	Rf	Bh	Hn	Mt	Uun	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
			Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium	
			140.12	140.91	144.24	(145)	150.36	151.96	157.25	158.92	162.50	164.93	167.26	168.93	173.04	174.97	
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	
			Thorium	Protactinium	n Uranium	Neptunium	Plutonium	Americium	Curium	Berkelium	Californium	Einsteinium	Fermium	Mendelevium	Nobelium	Lawrencium	
			232.04	213.04	238.03	(237)	(244)	(243)	(247)	(247)	(251)	(254)	(257)	(258)	(259)	(260)	
			Th	Ра	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
	Actinide Seri	es **															