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### Cross-references

Analytical techniques  
 Crystal field theory  
 Geochemical reference materials  
 Mineralogy  
 Petroleum: surface geochemistry  
 X-ray fluorescence (XRF)

## RHENIUM

### History and properties

In 1925, Noddack, Tacke and Berg discovered element number 75, which they named rhenium (Re). The silvery-white metal (hexagonal close-packed) has a density of 21 020 kg/m<sup>3</sup>, a melting point of 3453 K and boiling point (estimated) of 5900 K. In nature, the element has two isotopes, <sup>185</sup>Re (37.40 atom%) and <sup>187</sup>Re (62.60 atom%), and an atomic mass of 186.207. The isotope <sup>187</sup>Re decays to <sup>187</sup>Os by  $\beta^-$  emission (2.3 keV maximum  $\beta^-$  energy) with a decay constant of  $1.666 \times 10^{-11}$ /year, thus providing the basis for the Re–Os method of geochronology. Rhenium has oxidation states ranging from –1 to +7, but in nature +4 and +7 predominate.

### Cosmochemistry

The solar abundance is 0.0517 atoms Re per 10<sup>6</sup> atoms Si, corresponding to 36.5 ppb Re in CI chondrites. In planetary evolution, Re, like Au and the platinum group elements, is strongly siderophile (i.e. iron-loving) and is likely to be extracted almost quantitatively into the metallic core. This is illustrated by high abundances in iron meteorites (up to 5000 ppb; Pernicka and Wasson, 1987) and very low abundances in some unbrecciated achondrites (~0.002 ppb). In the early Earth, core formation similarly must have depleted the silicate mantle and the present mantle abundances of Re apparently results from a late influx of meteoritic material (Morgan, 1986).

### Igneous and metamorphic rocks

Undepleted regions of the Earth's upper mantle contain 0.26 ppb Re judging from analyses of spinel lherzolites. During basalt formation by partial melting, Re partitions into the melt and strongly correlates with S and Se. As a result, peridotites depleted in the basaltic fraction may contain as little as 0.003 ppb Re. Correspondingly, basalts are enriched relative to peridotite and both continental and oceanic varieties typically contain ~0.5 to 1.5 ppb Re. In other upper crustal rocks, the following abundances have been reported (in ppb Re): komatiites, 0.5–3; diabase, 0.42; andesite, 0.34; granite 0.22–0.56. Esser and Turekian (1993) estimated the average Re content of the upper crust to be 0.39 ppb. In lower crustal

rocks we find 0.37 ppb Re in granulite and 0.089 ppb Re in hornblende eclogite.

### Sedimentary rocks

Because of the solubility and stability of the perrhenate ion (ReO<sub>4</sub><sup>-</sup>), Re has a residence time in seawater of  $\sim 7.5 \times 10^5$  years and a present-day concentration of 8.2 ng/kg in open ocean water. Abundances are very low in oxidized sediments (ppb Re); shale, 0.009–0.051; quartz-rich sandstone, 0.021–0.034. In a euxinic regime, however, Re is reduced and is found highly enriched in sedimentary rocks (ppb Re), 28–184 in Black Sea sediments, 56–285 in black shales and up to 33 000 in mineralized black shales (Horan *et al.*, 1994).

### Economic geology

Rhenium may form its own sulfide in volcanic fumaroles (ReS<sub>2</sub> or Re<sub>2</sub>S<sub>3</sub>?), but economic occurrences are chiefly molybdenites or magmatic Ni–Cu ores. Molybdenites typically contain between 2 ppb and  $3 \times 10^6$  ppb Re (up to 11.5% in those from fumaroles). Re is commercially recovered from flue dust of molybdenite smelters. Magmatic Ni–Cu sulfide ores such as those from Noril'sk or Sudbury may have up to 500 ppb Re (Walker *et al.*, 1994). This may be recovered with the platinum metals in the anode sludge during electrolytic Cu refining.

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### Cross-references

Crystal field theory  
 Elements: platinum group  
 Elements: transitional  
 Geochronology and radioisotopes  
 Rhenium–osmium dating method

## RHENIUM–OSMIUM DATING METHOD

### General principles

The rhenium–osmium (Re–Os) dating technique is uniquely able to date directly sulfide minerals and some natural metals because both elements have strongly siderophile and chalcophile characteristics. Osmium has two isotopes that are variable in nature (Table R2). <sup>186</sup>Os is produced by the  $\alpha$  decay of <sup>190</sup>Pt, but isotopic variability is measurable only in materials with high Pt/Os ratios. The first <sup>190</sup>Pt/<sup>186</sup>Os data for sulfide

**Table R2** Isotopic composition of osmium and of the parents of its radiogenic isotopes rhenium and platinum

Isotopic mass	Isotopic abundance (atom%)		
	Rhenium	Osmium	Platinum
184	–	0.02	–
185	37.40	–	–
186	–	1.58*	–
187	62.60†	1.6‡	–
188	–	13.3	–
189	–	16.1	–
190	–	26.4	0.012¶
192	–	41.0	0.79
194	–	–	32.9
195	–	–	33.8
196	–	–	25.3
198	–	–	7.2

\* Radiogenic daughter of  $^{190}\text{Pt}$ .

† Parent of  $^{187}\text{Os}$  by  $\beta^-$  decay with half-life =  $41.6 \pm 0.1$  Ga.

‡ Radiogenic daughter of  $^{187}\text{Re}$ .

¶ Parent of  $^{186}\text{Os}$  by  $\alpha$  decay with half-life =  $450 \pm 7$  Ga.

ores and iron meteorites have been reported only recently and suggest a  $^{190}\text{Pt}$  half-life of  $450 \pm 7$  Ga (Walker *et al.*, 1997).  $^{187}\text{Os}$  results from the  $\beta^-$  decay of  $^{187}\text{Re}$ . The  $^{187}\text{Re}/^{188}\text{Os}$  ratio is very variable in rocks and in minerals ranging from zero in osmiridium to infinity in molybdenite ( $\text{MoS}_2$ ). In molybdenite, all  $^{187}\text{Os}$  is produced by decay of  $^{187}\text{Re}$  *in situ* and the model age,  $t$ , is given by:

$$t = \frac{1}{\lambda} \times \ln \left( 1 + \frac{^{187}\text{Os}}{^{187}\text{Re}} \right)_{\text{atom}}$$

$$= \frac{1}{\lambda} \times \ln \left( 1 + 1.591 \times \frac{^{187}\text{Os}}{\text{Re}} \right)_{\text{weight}} \quad (\text{R1})$$

where  $\lambda$  is the decay constant for  $^{187}\text{Re}$ .

Other materials that contain both Re and Os may be treated by plotting an isochron. Since

$$\left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{now}} = \left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{initial}} + \left( \frac{^{187}\text{Re}}{^{188}\text{Os}} \right)_{\text{now}} \times (e^{\lambda t} - 1), \quad (\text{R2})$$

plotting  $(^{187}\text{Os}/^{188}\text{Os})_{\text{now}}$  vs  $(^{187}\text{Re}/^{188}\text{Os})_{\text{now}}$  for a set of co-genetic materials yields a straight line with slope  $(e^{\lambda t} - 1)$  and with an intercept  $(^{187}\text{Os}/^{188}\text{Os})_{\text{initial}}$ .

### Half-life of $^{187}\text{Re}$

Measurement of the half-life of  $^{187}\text{Re}$  by counting techniques is difficult because of the low maximum  $\beta^-$  energy of 2.3 keV. Lindner and co-workers measured a half-life of  $42.3 \pm 1.3$  Ga by following over several years the growth of  $^{187}\text{Os}$  in purified perrhenic acid ( $\text{HReO}_4$ ). Very precise Re–Os isotopic measurements of iron meteorites yield a half-life of  $41.6 \pm 0.1$  Ga ( $\lambda = 1.666 \times 10^{-11}/\text{year}$ ; Smoliar *et al.*, 1995).

### Techniques

The application of the  $^{187}\text{Re}$ – $^{187}\text{Os}$  isotopic method has been fraught with analytical difficulties, which hampered development after the pioneering efforts of Herr and co-workers. Led by the work of Luck and Allègre in the early 1980s, renewed

interest in the Re–Os technique was sparked by the availability of techniques capable of measuring these elements at the nanogram level; secondary ionization mass spectrometry (SIMS), resonance ionization mass spectrometry (RIMS), induction-coupled plasma source mass spectrometry (ICP-MS). Negative thermal ionization mass spectrometry (NTIMS; Creaser *et al.*, 1991) has now become the technique of choice, however, since it measures Re and Os to the picogram level with high precision.

Abundances of Re and Os are best determined by isotope dilution, which requires addition to the weighed sample of isotopically enriched spikes (e.g.  $^{185}\text{Re}$  and  $^{190}\text{Os}$ ). Spike and sample isotopes must be equilibrated so that they follow each other exactly through the chemical purification. Ratios in the final isotopic mixture are measured and abundances are calculated by standard equations. For Re and Os, isotopic equilibration is not easy, particularly for Os which has complicated chemistry and is volatile (boiling point of  $\text{OsO}_4$ ,  $39.5^\circ\text{C}$ ). Three successful techniques are currently in use.

Alkaline fusion with  $\text{NaOH}$ – $\text{Na}_2\text{O}_2$  in a Zr crucible at  $\sim 600^\circ\text{C}$  achieves good isotopic equilibration and dissolves most geologic materials. Sample size is limited to  $\leq 0.6$  g and the Re blank of 20–50 pg may sometimes be prohibitive. An extraction by NiS fire assay is more suitable for materials low in Re and Os, for example, basalts and some sediments. In this technique a sample weighing several tens of grams is spiked and fluxed with a mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ , Ni and S. All Os and some Re may be recovered from the resulting NiS bead. Shirey and Walker (1995) describe a Carius (sealed thick-walled glass) tube method in which a sample weighing up to 4 g is digested in *aqua regia* at  $240^\circ\text{C}$  for 12 h. This method achieves good spike–sample equilibration and completely dissolves iron meteorites, sulfides, chromites and some ultramafic and mafic rocks. The technique is capable of low Re blanks ( $< 10$  pg) and will often be the chosen method.

### Applications

#### Meteorites

The Re–Os system is unique amongst the dating methods in that the elements are enriched in many iron meteorites. In some groups of magmatic irons, which formed cores of individual asteroids,  $^{187}\text{Re}/^{188}\text{Os}$  varies sufficiently due to fractional crystallization to define precise isochrons. With high precision measurements, subtle differences in the ages of iron meteorites are detected. The Re–Os isotope systematics of chondrites are less well determined, but carbonaceous chondrites and metal from ordinary chondrites have initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios at 4560 Ma that agree with the iron meteorite value of 0.0952 (Smoliar *et al.*, 1996).

#### Earth's mantle

Regions of the Earth's upper mantle undepleted by basalt formation contain 0.26 ppb Re and 3.4 ppb Os. That  $^{187}\text{Re}/^{188}\text{Os}$  ratio in the mantle is close to chondritic is confirmed by  $^{187}\text{Os}/^{188}\text{Os}$  in a wide variety of mantle-derived materials; osmiridium and other osmium-rich minerals, chromites from ophiolites complexes, peridotites from orogenic lherzolite massifs. NTIMS measurements of peridotite xenoliths suggest that primitive undepleted mantle (PUM) has a present day  $^{187}\text{Os}/^{188}\text{Os}$  of 0.1283, which closely resembles those of enstatite and ordinary chondrites, but is 1–2% more radiogenic than carbonaceous chondrites (Meisel *et al.*, 1996).

The mantle source region for mid-ocean ridge basalts (MORB) is slightly less radiogenic than PUM. The least altered abyssal peridotites from mid-ocean ridges have  $^{187}\text{Os}/^{188}\text{Os}$  of 0.1246 (Snow and Reisberg, 1995). In MORB themselves, Os is more radiogenic than in peridotites, but the measurements are subject to analytical difficulties due to low Os and  $\text{MnO}_2$  contamination.

The mantle beneath the continents, the sub-continental lithosphere (SCL), is less radiogenic than the MORB source mantle (Pearson *et al.*, 1995). The age of Re depletion is given by:

$$T_{\text{MA}} = \frac{1}{\lambda} \times \ln \left\{ \frac{\left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{Mantle}} - \left( \frac{^{187}\text{Os}}{^{188}\text{Os}} \right)_{\text{Sample}}}{\left( \frac{^{187}\text{Re}}{^{188}\text{Os}} \right)_{\text{Mantle}} - \left( \frac{^{187}\text{Re}}{^{188}\text{Os}} \right)_{\text{Sample}}} + 1 \right\} \quad (\text{R3})$$

When Re values are absent or suspect, minimum depletion ages,  $T_{\text{RD}}$ , may be derived by putting  $(^{187}\text{Re}/^{188}\text{Os})_{\text{Sample}} = 0$  in eqn (R3). Results show that Re depletion of the SCL began at least 3.5 Ga ago and that generation of crust and stabilization of the complementary SCL beneath it were closely linked.

In rocks related to thermal plumes originating deep in the Earth's mantle,  $^{187}\text{Os}/^{188}\text{Os}$  is often more radiogenic than PUM, suggesting a source with long term enrichment of  $^{187}\text{Re}/^{188}\text{Os}$ . In HIMU oceanic island basalts with  $^{187}\text{Os}/^{188}\text{Os} \approx 1.3\text{--}1.5$ , other isotope systems suggest that sources incorporated recycled ancient crust (Marcantonio *et al.*, 1995). In many other rocks derived from plumes, however, radiogenic  $^{187}\text{Os}/^{188}\text{Os} \approx 0.135\text{--}0.140$  is decoupled from other isotope systems, and is perhaps due to contamination of the plume source by the Earth's liquid outer core. By fractionational crystallization, formation of the Earth's solid inner core may have enhanced  $^{187}\text{Os}/^{188}\text{Os}$  in the liquid outer core by about 8% relative to chondrites to  $\sim 0.137$  (Walker *et al.*, 1997).

#### Earth's crust

During basalt formation by partial melting, Re partitions into the liquid, whereas Os remains predominantly in the residual peridotite. Accordingly, most igneous crustal rocks are characterized by high  $^{187}\text{Re}/^{188}\text{Os}$ . From deltaic and continental shelf sediments, and loess, average upper crustal abundances are estimated to be 0.39 ppb Re and 0.05 ppb Os, with  $^{187}\text{Os}/^{188}\text{Os} \approx 1.26$  (Esser and Turekian, 1993).

Some crustal rocks have been dated by whole-rock isochrons. Archean komatiite flows from the Abitibi Belt, Ontario, Canada give a Re–Os age of 2726 Ma, in good agreement with the Pb–Pb age of 2720 Ma. From Gorgona Island, Colombia, komatiites yield an age of 155 Ma and tholeiites were dated at 88 Ma (Walker *et al.*, 1991). Oxidized sediments are generally low in Re and Os but black shales may contain up to 1 ppm Re and 2 or 3 ppb Os. The Bakken, North Dakota, black shale from the Mississippian/Devonian boundary gives an isochron age of 354 Ma, agreeing with the accepted age of  $\sim 360$  Ma (Ravizza and Turekian, 1989).

#### Oceans

The behavior of Re in oxygenated ocean water is controlled by the stability of the perrhenate ion,  $\text{ReO}_4^-$ . Abundances below 400 m depth average  $7.42 \pm 0.04$  ng/kg normalized to a

salinity of 35‰. Above 400 m, Re contents are more variable, but generally follow salinity (Anbar *et al.*, 1992). Atlantic and Pacific water has 3.6 pg/kg Os (with an estimated error of  $\pm 10\%$ ), and  $^{187}\text{Os}/^{188}\text{Os}$  of  $1.04 \pm 0.03$  (Sharma *et al.*, 1997). In most organic-rich marine sediments, the hydrogenous component (i.e. that derived from the seawater) has an average  $^{187}\text{Os}/^{188}\text{Os}$  of  $1.00 \pm 0.04$ , but for the enclosed Black Sea, the hydrogenous component has  $^{187}\text{Os}/^{188}\text{Os} = 0.85 \pm 0.07$ . In a long core from the North Pacific, the hydrogenous component shows an almost monotonic increase in  $^{187}\text{Os}/^{188}\text{Os}$  from 0.384 at 58 Ma to a present day value of 1.03 (Pegram *et al.*, 1992).

Measurements of  $^{187}\text{Os}/^{188}\text{Os}$  in sewage and sediments provides a useful tracer to the origin of pollutants. Anthropogenic Os originates from the extensive use of this metal in research and may also be a byproduct of automobile exhausts which emit substantial amounts of Pt (Ravizza and Bothner, 1996).

#### Economic geology

Molybdenites rich in Re occur in many felsic rock systems but there are few published age studies since the early work of W. Herr and co-workers. Molybdenites from base-metal porphyry ore deposits in south-western North America have ages that fall into two groups, 55–60 Ma and 70–74 Ma. Precisions range from  $\pm 0.6\%$  to  $\pm 3.2\%$ , which are as good as, or better than, K–Ar ages of co-existing minerals (McCandless and Ruiz, 1991). Ages of similar precision have been reported for molybdenites from China and Japan. Very precise Re–Os molybdenite ages of  $1486 \pm 5$  Ma for the Kabeliai prospect, Lithuania and  $2780 \pm 8$  Ma for the Kuittila prospect, Finland are in agreement with zircon U–Pb ages (Stein *et al.*, 1998).

Sulfides other than molybdenite may contain significant amounts of both Re and Os. Isochrons for the Sudbury, Ontario, igneous complex – an ancient ( $1850 \pm 1$  Ma) impact structure that is a major source of Ni–Cu sulfide ores – yield good ages and high initial  $^{187}\text{Os}/^{188}\text{Os}$  strongly suggesting a largely crustal origin for Os. Magmatic Ni–Cu ores at Noril'sk, Siberia are associated with the plume-derived Siberian flood basalts. Isochron ages of  $245.7 \pm 0.6$  Ma and  $247.0 \pm 3.8$  Ma for the ores are in good agreement with the ages of the intrusions by other methods. For Rankin Inlet Ni ores, isochrons yield acceptable ages and the radiogenic initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios are clear evidence of crustal contamination from local metasediments. In the late Archean terranes of Western Australia, sulfide ores and komatiite yield an isochron age of  $2706 \pm 36$  Ma and an initial  $^{187}\text{Os}/^{188}\text{Os}$  close to chondritic, suggesting no significant contribution from sulfidic sediments (Foster *et al.*, 1996). Initial  $^{187}\text{Os}/^{188}\text{Os}$  ratios in high-Os, low-Re minerals (chromite, osmiridium, erlichmanite, etc.) range from chondritic to values as radiogenic as 0.25 in such layered complexes as the Bushveld and Freetown, Sierra Leone (Hattori *et al.*, 1991). A detailed study of the Stillwater complex indicates several stages of magma mixing between a U-type magma derived from subcontinental lithospheric mantle and A-type magma that incorporated radiogenic Os from early Archean crust (Lambert *et al.*, 1995).

Isotope systematics of mineralized black shales from China and Canada show that enrichment of Re and Os occurred near the time of sedimentation (Horan *et al.*, 1994).

#### Conclusion

The Re–Os isotopic method has come into general use only since the introduction of the NTIMS method of isotopic analysis. A wide range of applications has been developed, and this

isotopic system is in demand by the mining industry. The value will be enhanced by the future development of the Pt–Os method.

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## Cross-references

Dating methods  
 Geochronology and radioisotopes  
 Geologic time scale  
 Radioactivity

## RHODIUM

Rhodium, Rh, was discovered in 1803. Its name is derived from *rhodon*, meaning rose, the color of aqueous solutions of its salts. Rhodium has an atomic weight of 102.91 and an atomic number of 45. It is a hard, silver-white metal. Table R3 lists some of its physical properties.

**Table R3** Physical properties of rhodium

Density (at 20°C) (g/cm <sup>3</sup> )	12.4
Melting point (°C)	1960
Boiling point (°C)	3700
Specific heat at 0°C (cal/g/K)	0.0589
Crystal lattice	face-centered cubic

Rhodium is a member of the platinum metals group which includes platinum, palladium, iridium, ruthenium and osmium. Its chemical properties resemble those of iridium. At 600°C in air, a gray oxide film of Rh<sub>2</sub>O<sub>3</sub> forms on the surface of the metal. Rhodium is attacked at temperatures above 500°C by a number of elements including lead, mercury, zinc, tin, chlorine, fluorine and sulfur. In its chemical compounds, rhodium exhibits oxidation states of +2, +3, +4 and +6, the +3 state being the most common. Boiling sulfuric acid and hot hydrobromic acid dissolve rhodium sponge. The same acids attack the bulk metal slowly. Rhodium is dissolved in fused alkali bisulfates, and in fused alkali containing an oxidant.

The average abundance of rhodium in the continental crust is 0.001 ppm. Rhodium is found together with the other platinum group elements in deposits of the platinum metals. The main elements are platinum and palladium, while rhodium and the remaining three minor elements comprise about 10% of the total platinum metals. The main sources of rhodium are the Merensky Reef of the Bushveld Complex, South Africa, the nickel–copper sulfide deposits of the Noril'sk region, Russia, and of the Sudbury region, Canada, and the Stillwater Complex, USA (Naldrett, 1981). Some rhodium minerals are listed in a glossary of minerals of the platinum group elements (Cabri, 1981). World production of rhodium was about 3% of the total 280 900 kg for platinum metals (*Minerals Yearbook*, 1992).

Complex procedures are followed in processing ores and concentrates containing platinum metals (Benner *et al.*, 1991). Rhodium in ores, rocks and soils is determined after extraction and concentration of the platinum group elements by fire assay methods. Concentrations of rhodium in lead or nickel sulfide fire assay beads are measured by techniques such as instrumental neutron activation analysis, atomic absorption spectrometry and inductively coupled plasma-atomic emission or -mass spectrometry (Van Loon and Barefoot, 1991). Rhodium is